Elementary

Chemistry

Linebarger

ELEMENTARY

CHEMISTRY

By

C. E. LINEBARGER

Instructor in Chemistry in the
Lake View High School, Chicago,
and Editor of "School Science"

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THE PREFACE

A COURSE in elementary chemistry suitable for the average high-school student should give a description of the common elements, their compounds, and their reactions, sufficiently clear and full to enable him to form correct conceptions of the nature of the changes that are going on around him. But it should do more ; as far as is possible in an elementary course, it should provide him with a thorough groundwork in the simpler laws and theories of modern chemistry. This gives meaning and coherence to what would otherwise be fragments of knowledge, and lays a solid foundation for the continuation of the study of chemistry.

The descriptive matter should impose as little strain as possible on the student's memory. To accomplish this the facts should be properly coördinated with one another and duly correlated with the experiences of everyday life. General points of view should be emphasized and isolated details suppressed. Important historical items should be mentioned, for they put life into the subject and give it perspective.

The laws of chemistry should be introduced in immediate connection with the discussion of those substances which first present typical applications of each law. The treatment of the laws should be full and varied. Reference to them should be made frequently throughout the course, so that they may become a permanent working possession of the student.

The modern theories of physical chemistry should receive the attention their importance demands. They are indeed no longer modern, for they have stood the

test of time.   While anything like a thoroughgoing treatment is, of course, impracticable in an elementary text, yet the explanations which these theories suggest in regard to phenomena may in several instances be given with profit.

Industrial chemistry demands recognition, and although it may not be feasible to enter into a full discussion of many industrial processes, yet the details of a few should certainly be given, so that the outlines of others may be the more readily understood.   The best way to get adequate notions of industrial operations is by excursions to works.   But the description of a process, accompanied by diagrams designed to bring out the important features and the general run of the process, assists in preparing students for excursions. They are thereby saved from being overwhelmed by the mass of detail presented on inspection of a plant; they recognize its salient features more readily; they know for what to look and how to look; they correctly grasp the connection between the industrial operations and the underlying chemical principles.

The energy aspect of chemistry should not be entirely neglected.   Elementary notions of thermochemistry illustrated by simple reactions should be dwelt upon here and there in the course.

Theories should not be considered until after the student has acquired some knowledge of the facts and laws of chemistry.   Their presentation should be such as not to fail to give correct notions of their real value and their relation to facts and laws.

The purpose of exercises and problems is not merely to test the memory, but rather to develop power of constructive thought and creative imagination.   The exercises should be so selected and worded that their answers are not found explicitly stated in the preceding

chapter. A comparison of facts and an exercise of judgment should be required in framing the answers. Most of the problems should be taken directly from the works of the pioneers in chemical investigation, and should be chosen more for their chemical than for their mathematical value.

Laboratory and text-book work should go hand in hand. In certain parts of the subject the laboratory has to be subordinated to the class room, and in others, the class room to the laboratory. But, all in all, the closest correlation possible should be maintained between the two. The experiments should be simple but not trivial. Each one should lay special emphasis upon but a single point. A reasonable amount of simple quantitative work involving the careful manipulation of simple apparatus will help to develop the power of observation and to prevent slovenliness in the laboratory.

No amount of written description and sectional drawings can make the secondary-school pupil see how his apparatus should be put together so well as a photograph. Hence an elementary text-book should be illustrated in the most graphic manner. The author believes that a photograph of the apparatus the pupil is to handle furnishes a better illustration than the sectional drawings commonly used in science text-books. Most of the illustrations in this book have been secured by setting up the actual apparatus, photographing it, and then silhouetting it in the half-tone plates. Where internal construction needs to be shown the sectional drawing has been used as before.

Believing that these are the requisites of a practical elementary text-book in chemistry, the author has attempted to meet them in the preparation of this work. He has aimed to economize teaching energy

and to provide for flexibility of the course. With that end in view he has made the typographical arrangement such that certain topics may be readily omitted without interfering with the continuity of the course. Not that he feels that such topics should be omitted, but because he recognizes the need which frequently arises for shortening the course, and wishes to indicate what may be omitted with least loss.

The author takes pleasure in thanking the following teachers for valuable criticisms on the manuscript: Mr. Harry D. Abells, *Morgan Park Academy, Morgan Park, Ill.;* Dr. C. E. Boynton, *Robert Waller High School, Chicago;* Miss Louella Chapin, *South Division High School, Chicago;* Mr. Harry Clifford Doane, *Central High School, Grand Rapids, Mich.;* Mr. Oscar R. Flynn, *Hyde Park High School, Chicago;* Mr. Albert C. Hale, *Boys' High School, Brooklyn, N. Y.;* Prof. Alexander Smith, *The University of Chicago;* Mr. Charles M. Turton, *South Chicago High School, Chicago;* Prof. Theodore Whittelsey, *Northwestern University;* Mr. C. M. Wirick, *R. T. Crane Manual Training High School, Chicago;* Mr. E. C. Woodruff, *Lake View High School, Chicago;* and Mr. F. J. Watson, *William McKinley High School, Chicago.*

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C. E. LINEBARGER.

Chicago, April, 1904.

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GEORG ERNST STAHL

1660-1734; German

*Developed Becher's hypothesis of
phlogiston so as to apply to all
branches of chemistry*

JOHANN JOACHIM BECHER

1635-1682; German

*First proposed the explanation
of the phenomena of combustion
known as the Phlogiston Theory*

TORBERN BERGMAN

1735-1784; Swede

*Contributed largely to the knowl-
edge of chemical facts and pro-
cesses, and to industrial appli-
cations of chemistry*

JACQUES ALEXANDER CÉSAR CHARLES

1746-1822; French

*Ascertained relationship between
volume (or pressure) and temper-
ature of gases. First to make
balloon ascensions*

ROBERT BOYLE

1626-1691; English

*Proved inverse relationship be-
tween pressure and volume of
gases. Introduced use of indi-
cators in chemistry*

Plate I

BECHER STAHL

BERGMAN

BOYLE CHARLES

Plate I

ELEMENTARY CHEMISTRY

CHAPTER I

INTRODUCTORY

1. Nature. Nature is the name given to the multitude of objects all about us. These have different properties and are perpetually changing. Man has a firm belief founded in experience that there is a constancy in the way things happen — that the same causes acting under the same conditions always produce the same effects. This constancy gives rise to the Laws of Nature, according to which the phenomena, *i. e.*, the happenings of nature, occur. A *Law of Nature* is a concise statement covering a large range of phenomena; it is a general fact embracing a multitude of individual facts. Man often tries to explain phenomena by means of hypotheses upon which theories may be built. A collection of certain of the Laws of Nature, together with the facts and theories pertaining to them, constitutes a *Branch of Science*.

2. Science. Science is classified knowledge, or "the knowledge of many, methodically arranged and digested so as to be attainable by one." Men are continually investigating nature and communicating their discoveries to others. The facts found are compared, sifted, and arranged. Certain groups

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of facts present such uniformity of relationships as to be expressible in a brief statement — a Law of Nature. Points of view are obtained which bring the facts and the laws pertaining to them into such connection that the labor of learning them is lightened. The contents of this book are gleanings from the work of many men of many countries throughout many years. The facts, laws, and theories are presented in what is thought to be the order best adapted for their comprehension.

3. Matter and Energy. Chemistry, as well as all other so-called physical sciences, has to do with *matter* and *energy*. Matter may be defined as that which *occupies space*, and when one portion of matter *does work* upon a second, it is said to possess energy. We get our knowledge of the properties of matter through the medium of our senses, and matter cannot act upon our senses unless it possesses energy. A definite portion of matter is called a *body*. The kinds of matter composing bodies are called *substances*. Thus, a "lead" pencil is a body made up of the two substances, wood and "lead."

The amount of matter in a body is called its *mass*. Two bodies are said to have equal masses when the attraction between each one of them and a third body is the same. If the third body is the earth, the attraction is called *gravity*, and the two bodies are said to have the same *weight*. Mass is a property inherent in a body and is independent of other bodies; weight is the attraction between bodies and the earth. Under fixed conditions mass and weight are proportional, *i. e.*, they increase or decrease in the same way.

4. What We Study in Chemistry. First of all, we observe the properties of the different kinds of matter. Thus, suppose we wish to make a chemical study of the substance known as roll sulfur or brimstone. By our sense of sight we learn that it is yellow and opaque; our sense of touch teaches us that it is brittle and rather hard; our senses of taste and smell are not affected by it and we hence conclude that it is tasteless and odorless. We further observe that if it is rubbed against a piece of woolen cloth it will attract bits of paper and other light substances; it becomes electrified, we say. When we heat it in the air, it melts, takes fire, and burns with a blue flame and stifling odor. And so we could go on accumulating fact upon fact and thus increase our knowledge of sulfur. By appropriate experiments we can in a similar manner get a knowledge of every other substance.

But it is also in the province of chemistry to study the changes and transformations that substances undergo. Thus, when sulfur burns it is completely converted into a gaseous substance whose most striking property perhaps is its stifling odor. We must study the conditions of such changes and ascertain what other substances help in bringing about the changes. Also, the energy manifested as heat during the burning of sulfur, and, in general, all the changes of energy accompanying changes in substances, are to be considered.

Further, in the study of the properties and changes of substances, certain similarities and regularities are sometimes observed whose generalized

statement leads to the Laws of Chemistry.   And man's ingenuity and imagination are often stimulated to attempt explanations of the facts discovered about substances, and these explanations form the hypotheses and theories of chemistry.

5.   **Physical and Chemical Changes.**   The two metals, platinum and magnesium, behave very differently when heated in the air.   The platinum may become hot enough to emit light, but when it is cool it assumes its original appearance.   It has undergone only *physical changes*, as expansion and incandescence.   When, on the other hand, the magnesium is heated, it burns with a dazzling light and is changed into a loose, white mass; a *chemical change* has occurred.

When a current of electricity is sent through a wire, the latter is heated, and with strong enough current may become so hot as to glow and even to melt.   But when a current of electricity passes through a solution of copper sulfate (blue vitriol), the solution not only becomes heated, but also copper is deposited on the solid by which the current leaves the solution.   The first phenomenon is an example of a *physical*, the second of a *chemical change*.

Experiments similar to the above may be multiplied almost indefinitely.   They all go to show that among the innumerable changes in nature there are some which are superficial and do not bring about any profound alterations in the substances concerned, while there are others in which the changes are considerable and deep-seated.   But there are also many changes which lie between

true physical and chemical changes, and the distinction is often but slight and arbitrary. Still, it is useful and hence may be retained.

6. Physical and Chemical Properties. The properties of substances studied with respect to their physical changes are called physical. Important among such properties are *color*, *taste*, *smell*, *hardness*, *solubility*, etc. Many physical properties can be expressed numerically. Thus, an important physical property of a substance is its *density*—the mass of unit volume of it. For example, one cubic centimeter of sulfur weighs 2ᵍ· The density of sulfur may therefore be expressed by the number 2. The temperature at which a solid turns into a liquid—its *melting point*—is also an important physical property; likewise the temperature at which a liquid boils—the *boiling point*. Such numerical data are known as *physical constants*.

The chemical properties of substances are those involving chemical change. Thus, it is a chemical property of sulfur to burn with a blue flame and give off a gas of stifling odor.

7. The Identification of Substances. The number of properties which a substance may have is very great, and the question arises: How many properties of a substance must be known to distinguish it from every other substance? Experience has shown that if samples of substances exactly resemble one another in a few (a half-dozen or even less) properties, they will resemble one another in all others. This simplifies the identification of substances greatly, and it is one of the objects of chemistry to find out the least number

of properties needed to identify substances. The identity of a substance is established by means of *tests*.

8. Tests. By subjecting a substance to the action of other substances under certain conditions and comparing the results with known and recorded properties we make a *test*. The property which is most characteristic of a substance is, whenever possible, chosen as its *test*. Thus, the burning of sulfur, with its blue flame and stifling odor, is ordinarily sufficient to establish the identity of that substance. Additional *confirmatory tests*, however, are usually employed so as to make the identification surer. Thus, the color, solubility, and electrification of sulfur may be employed as tests to confirm its identity.

9. Chemical Action. Chemical changes are commonly called *reactions*. The substances which react are called *reagents* or *factors*, and the substances resulting from the reaction, *products*. Chemical reactions take place under a great variety of conditions. Oftentimes it is necessary to employ heat or electricity — sometimes light — to start the reaction, although in numerous instances the mere bringing together of the reacting substances at ordinary temperatures is sufficient. It is seldom possible to bring solid substances near enough together by mere mechanical mixing to cause the desired reaction. This, however, may be facilitated by solution, fusion, pressure, or volatilization. To ascertain the best conditions for carrying out a reaction is one of the most important tasks that the chemist has to undertake.

10. The Cause of Chemical Change. Why certain substances when brought together undergo no great change even when heated, while others react with great vigor and yield products of totally different properties, we do not know. The cause of chemical change is hard to find. We can, indeed, say that some substances have a "chemical affinity" or "chemism" for one another, but this really does not mean much and explains nothing. Yet just as there is a something which causes all portions of matter to gravitate towards one another, so is there a something which causes certain substances to undergo chemical change under proper conditions. While we are at present unable to understand what this something is, still we can try to ascertain how it acts; we can, at least, investigate the actions and reactions of substances upon one another.

11. Elements and Compounds. The diversity of nature is infinite. The number of substances is unlimited. But science begins with classification. The first classification of chemistry is that which divides all substances into *elements* and *compounds*. To ascertain whether a substance is an element, chemists proceed as follows: They take a definite weight of it and subject it to all possible changes, keeping strict account of the weights of the factors and products in all the reactions studied; if in all these changes the whole of it has not been converted into another substance weighing less than the original substance, they conclude it is an element. Thus, iron may be made to react with a large number of substances to give rise to other substances, not one of which, however, has been found to

weigh less than the iron taken. Iron is therefore
an element.

An *element* then is a substance, a given weight
of which has never *all* been changed into another
substance weighing less than the original. All
other substances are composed of elements; they
are called *compounds*. The existence of nearly
eighty elements has been established; the number
of compounds is limitless.

NOTE. Some substances which were at one time supposed to
be elements have later been found to yield simpler substances,
and it is quite possible that some of the elements of to-day have
no right to the name. It should be borne in mind that the term
"element" is but relative and depends upon the state of our
knowledge and skill.

The exact number of elements is doubtful, for we cannot be
sure that certain substances now regarded as elementary will not
ultimately prove to be compound, and also because but a relatively
thin layer of the earth has been subjected to examination.

12. Metals and Non-Metals. It has been found
convenient to classify elements into metals and
non-metals, although in several cases it is difficult
to decide to which class an element belongs.
Metals have a peculiar "metallic" luster and are
good conductors of heat and electricity; they are
opaque and with the exception of mercury are solid
under ordinary conditions; most of them are mal-
leable and ductile; *i. e.*, they can be hammered or
rolled into sheets and drawn out into wire. Non-
metals do not have a "metallic" luster and are poor
conductors of heat and electricity; several of them
are gaseous under ordinary conditions. The chem-
ical differences between metals and non-metals will
be considered in connection with each element.

TABLE OF THE ELEMENTS[1]

METALS

Aluminum
Antimony
Arsenic
Barium
Beryllium
Bismuth
Cadmium
Cæsium
Calcium
Cerium
Chromium
Cobalt
Copper
Erbium
Gallium
Germanium
Gold
Indium
Iridium
Iron
Lanthanum
Lead
Lithium
Magnesium
Manganese

Mercury
Molybdenum
Neodymium
Nickel
Niobium
Osmium
Palladium
Platinum
Potassium
Praseodymium
Radium
Rhodium
Rubidium
Ruthenium
Samarium
Scandium
Selenium
Silver
Sodium
Strontium
Tantalum
Tellurium
Thallium
Thorium ·
Tin
Titanium

Tungsten
Uranium
Vanadium
Ytterbium
Yttrium
Zinc
Zirconium

NON-METALS

Argon
Boron
Bromin
Carbon
Chlorin
Fluorin
Helium
Hydrogen
Iodin
Krypton
Neon
Nitrogen
Oxygen
Phosphorus
Silicon
Sulfur ·
Zenon ·

HISTORICAL NOTE. The conception of an element as just given was gained towards the end of the eighteenth century and is mainly due to the French chemist, Lavoisier. Prior to that time it was held that there were four "elements"— fire, water, air, and earth —and that the properties of substances depended upon the proportions of these "elements" which they were supposed to contain. This doctrine dates from very ancient times and was arrived at, not by an investigation of nature but by philosophical speculation alone. It is indeed in accord with a superficial view of phenomena, but cannot stand the test of a stricter scrutiny.

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[1] The more important elements are in italics.

For example, water acted upon by heat (fire) changes into vapor (air) and leaves an earthy (earth) residue. What more natural than to conclude that water, through fire, changes into air and earth? But even a slight experimental examination shows that water does not cease to be water upon vaporization, for the vaporized water may be condensed again into the liquid form, and also that the earthy residue is due to the presence of solid substances previously dissolved in the water.

This may serve as an instance of the mode of reasoning during the reign of the four elements. When men abandoned speculation and entered upon thoroughgoing investigation, endeavoring to account for everything in a phenomenon, especially the changes of weight, the progress of chemical science was rapid.

13. Mixtures and Compounds. Most substances occurring in nature are made up of several others. Granite, for instance, contains three or more different minerals. If the constituents of a substance can be separated by mechanical processes, as by picking them out or dissolving them out, they are said to form a *mixture*. If, however, mechanical processes are inadequate in effecting a separation, we have to do with a *compound*.

ILLUSTRATIVE EXAMPLE. Mixtures of powdered sulfur and iron may be prepared in all proportions. A magnet stirred about in the mixture will pick out the iron, and a liquid, carbon bisulfid, will dissolve out the sulfur. These means of separation are purely physical, and we have to do with a mixture. When a mixture of fifty-six parts by weight of iron and thirty-two parts of sulfur is heated in a flame it begins to glow at a certain temperature, and enough heat is evolved to keep the mixture incandescent for some time, even after the flame is removed. A chemical change has taken place. We now find on applying the magnet and the carbon bisulfid that the product is much less magnetic and nearly insoluble. A compound of iron and sulfur has been formed.

14. Differences Between Mixtures and Compounds. In the preparation of mixtures but little energy, and that mechanical, is required, while in the preparation of compounds the changes of energy are considerable. Also the properties of a mixture are about the average of the properties of its constituents. But the compound usually has totally different properties from those of the elements composing it. There is ordinarily as much difference between the compound and each one of its constituents as there is between the elements themselves entering into its composition. This profound alteration of properties is characteristic of a chemical change. Further, compounds are characterized by having an invariable composition. Only so much sulfur can combine with so much iron, and an excess of either element present does not enter into reaction. To ascertain as accurately as possible what these *combining proportions of the elements* are is one of the fundamental problems of chemistry.

To sum up, compounds differ from mixtures in that:

1. They have constant physical properties different from those of their constituent elements.

2. Not inconsiderable amounts of heat or other forms of energy are made manifest in their formation.

3. They have an invariable composition.

15. Conservation of Matter and Energy. The chemical and physical changes of substances involve primarily changes of mass and energy. It has been found that even in the most complicated

changes, if strict account be kept of all the amounts of matter and energy that undergo transformation, these always foot up to the same sum total. *Neither matter nor energy can be created or destroyed.*

These facts of experience have led to the establishment of two grand laws which pervade all the physical sciences: the Law of the Conservation of Energy and the Law of the Conservation of Matter. These two laws are of fundamental importance and apply to every physical and chemical change.

16. The Immutability of the Elements. While there are about eighty elementary kinds of matter, there are only a half-dozen or so of different kinds of energy, as mechanical, chemical, electrical, etc. These different kinds of energy may, with certain restrictions, be converted into one another. Such is not the case, however, with the different kinds of elementary substances. While mechanical energy may be converted into electrical or heat energy, lead or copper cannot be changed into gold.

This immutability of the elements has not always been recognized; indeed, up to the end of the eighteenth century one of the principal aims of chemistry (or alchemy, as it was then called) was to devise means to convert cheap materials into the valuable metals, silver and gold.

HISTORICAL NOTE. To Lavoisier belongs the credit of having been the first clearly to enunciate and vigorously to emphasize the Law of the Conservation of Matter. The Law of the Conservation of Energy was not stated until a little more than a half-century later, when Mayer, Helmholtz, and Joule announced it independently.

IMPORTANCE OF CHEMISTRY. Chemistry has not only great value as a means of mental discipline, but also great usefulness in supplying the needs of man. By its aid many products which were formerly thrown away are now rendered useful, and its discoveries are now applied to practical use in medicine, agriculture, and in nearly every great manufacturing industry. Chemistry is also a fundamental science upon which certain other sciences, as biology, physiology, and mineralogy, are to a considerable extent based.

Exercises

1. How would you make a chemical study of coal?

2. State the kind of change in each of the following: (*a*) the burning of wood, (*b*) the melting of ice, (*c*) the welding of iron, (*d*) the rusting of iron, (*e*) the tarnishing of silver.

3. Give as many physical and chemical properties as you can of the following substances: Gold, silver, lead, tin, copper.

4. Which of the properties found in answer to the previous exercise will best serve as tests?

5. How have chemists come to the conclusion that iron is an element?

CHAPTER II

THE GENERAL PROPERTIES OF GASES

17. States or Conditions of Matter. Any definite kind of matter can be made to assume three more or less clearly defined states, merely by the alteration of the relative amounts of energy it contains in the form of heat. Thus, water may be converted into ice by the withdrawal of heat, and into steam by the addition of heat; the freezing and boiling of water take place under fixed conditions of temperature and pressure. In general, then, a substance may be obtained in the solid, liquid, or gaseous state by suitable adjustment of temperature and pressure, and it is the relative amount of heat energy contained in it which determines its state of aggregation.

A *solid* has a *definite shape* and a *definite volume.*

A *liquid* has a *definite volume,* but takes the shape of the vessel containing it. Its free surface, *i. e.,* the surface not in contact with a solid, is horizontal.

A *gas* has *neither shape nor volume* of its own; these depend upon the shape and the volume of the containing vessel. A gas spreads out and fills any space offered it.

A rise of temperature has the same effect upon matter in all three states; with but few exceptions substances increase in volume when heated. Solids change the least, liquids more, and gases most. Also, an increase of pressure diminishes the volume of substances in all three states.

18. The Necessity for a Preliminary Study of Gases. We know far more about the gaseous state than about the liquid or solid states, and chemistry is to a large extent built upon facts derived from the study of gases. As the first elements we shall study are gases and form gaseous or volatile compounds, it is necessary that we acquire beforehand a knowledge of the general properties of gases. This belongs properly to the · subject of physics, but it is so necessary for a comprehension of chemistry that it must also be given here.

19. Volume, Pressure, and Temperature. In chemistry, volumes are measured usually in cubic centimeters ($^{c.c.}$) or in liters ($^{l.}$). (See Appendix *B*.)

Pressures are measured in atmospheres or in millimeters ($^{mm.}$) of mercury. The air presses down upon the earth's surface on an average so as to balance at the level of the sea a vertical column of mercury 760$^{mm.}$ high, and this pressure is defined to be the standard pressure of one atmosphere.

Temperatures are measured by mercury-in-glass thermometers graduated according to the centigrade scale. (See Appendix *C*.) The zero corresponds to the temperature of melting ice and the 100° point to the temperature of water boiling under standard pressure. The one hundredth part of this fundamental interval is set equal to one degree, and the value of a degree thus determined is extended above and below these fixed points.

20. Charles' Law. *All gases under constant pressure expand equally for like changes of temperature.*

Thus, it has been found that one liter of a gas measured at 0° becomes:

$(1 + \dfrac{1}{273})$ liters at $1°$; $(1 + \dfrac{2}{273})$ liters at $2°$;

$(1 + \dfrac{3}{273})$ liters at $3°$; $(1 + \dfrac{4}{273})$ liters at $4°$;

$(1 + \dfrac{5}{273})$ liters at $5°$; $(1 + \dfrac{t}{273})$ liters at $t°$;

and

$(1 - \dfrac{1}{273})$ liters at $-1°$; $(1 - \dfrac{2}{273})$ liters at $-2°$;

$(1 - \dfrac{3}{273})$ liters at $-3°$; $(1 - \dfrac{t}{273})$ liters at $-t°$.

21. Absolute Temperatures. A given mass of any gas which at $0°$ occupies $273^{c.c.}$ will have at $100°$ a volume of $(273+100) = 373^{c.c.}$, and at $-100°$ a volume of $(273-100) = 173^{c.c.}$. At $-273°$, therefore, the volume of the gas would be $(273-273) = 0^{c.c.}$, *i. e.*, it would be reduced to nothing. Such a conclusion is manifestly absurd, and, as a matter of fact, all gases are condensed into liquids and solids before such a low temperature is reached. If $-273°$ be taken as a starting point and the centigrade value of a degree be retained, a thermometric scale will be obtained on which the readings are directly proportional to the volumes of the gas. Such a scale is called the *absolute scale*, and $-273°$ is known as the *absolute zero*. Centigrade readings of temperature are converted into absolute readings by adding 273 to the former, thus:

$$273° \ (absolute) \ = \ 0° \ (centigrade),$$
$$274° \qquad \text{``} \qquad = \ 1° \qquad \text{``}$$
$$270° \qquad \text{``} \qquad = -3° \qquad \text{``} \qquad \text{etc.}$$

LAVOISIER

SCHEELE

PRIESTLEY

CAVENDISH

BLACK

Plate II

CARL WILHELM SCHEELE

1742-1786; Swede

Discovered oxygen, chlorin, am-
monia, manganese, and many
acids. Devised methods of prep-
aration for many substances

ANTOINE LAURENT LAVOISIER

1743-1794; French

Showed role oxygen plays in com-
bustion phenomena. Propounded
the Law of the Conservation of
Matter

JOSEPH PRIESTLEY

1733-1804; English

Discovered oxygen and several
other gases. Devised methods
for handling and storing gases

JOSEPH BLACK

1728-1799; English

First prepared carbon dioxid in
isolated state. Introduced more
definite notions about gases

HENRY CAVENDISH

1731-1810; English

Discovered hydrogen and compo-
sition of water. Determined
composition of the air

Plate II

22. Boyle's Law. *If the temperature of a gas be maintained constant, its volume varies inversely as its pressure.*

Thus, if the pressure is doubled, the volume is half as large; if the pressure be reduced to one-third, the volume is trebled, and so on.

23. Density and Specific Gravity. The *density* of a substance is the mass of unit volume of it; its *specific gravity* is the ratio of the weight of a given volume of it to the weight of an equal volume of another substance taken as a standard. Two stand-ards are in use for gases — air and hydrogen — while water is the standard for liquids and solids. The weights of one liter of hydrogen and of air at 0° and 760 $^{mm.}$ of mercury are 0.09$^{g.}$ and 1.293$^{g.}$ respectively. With hydrogen as standard, the specific gravity of air is 1.293/0.09 = 14.37, while with air as standard, the specific gravity of hydrogen is 0.09/1.293 = 0.069.

NOTE. It is unfortunate that two standards are in use. Hydro-gen is the standard used in this book, and, unless stated to the contrary, specific gravities will be referred to hydrogen.

The term *vapor density* is often used to distinguish the specific gravity of a substance in the gaseous or vaporous state from that which it may have in the liquid or solid condition.

24. Standard Conditions. When the weights of a liter of air and of hydrogen were given (§ 23) both the temperature and the pressure were speci-fied. This is necessary in all cases, for the volume that a given mass of gas occupies depends upon its pressure and temperature. In comparing the weights of the volumes of ·gases, both the tem-perature and pressure must be stated, or at least

3

understood. Chemists have agreed to give the weights of gases with their volumes at the standard temperature of $0°$ ($273°$ on the absolute scale) and at the standard pressure of one atmosphere. The reduction of the volumes of gases measured at other temperatures and pressures than these standard conditions may be effected by the application of the laws of Boyle and Charles. They may be applied separately or in combination.

25. Reduction of the Volume of a Gas to Standard Pressure. Suppose we have v liters of a gas under a pressure of p $^{mm.}$ of mercury, and wish to find its volume v' at 760 $^{mm.}$ of mercury. Boyle's Law permits us to write the proportion:

$$\frac{v}{v'} = \frac{760}{p}$$

Whence,

$$760 \, v' = p \, v$$

and

$$v' = v \, \frac{p}{760}$$

In words: *To reduce the volume of a gas to standard pressure, multiply the given volume by a fraction whose denominator is always 760 and whose numerator is the given pressure.*

26. Reduction of the Volume of a Gas to Standard Temperature. Suppose v_1 liters of a gas to have been measured at the temperature of $t°$, and that it is required to find its volume, v'_1 at $0°$, *i. e.*, $273°$ on the absolute scale. By Charles' Law we have:

$$\frac{v_1}{v'_1} = \frac{273+t}{273}$$

Whence,

$$(273 + t)\ v'_1 = 273\ v_1$$

and

$$v'_1 = v_1\ \frac{273}{273 + t}$$

In words: *To reduce the volume of a gas to standard temperature, multiply the given volume by a fraction whose numerator is always 273 and whose denominator is 273 plus the given temperature,* i. e., *the absolute temperature.*

27. Reduced Volumes. This is an elliptical expression for volumes reduced to 0° and 760 $^{mm.}$ of mercury. As Boyle's and Charles' Laws are independent of each other, the reductions to standard conditions may be made independently; that is, we may suppose the pressure constant and reduce to standard temperature, and then suppose the temperature constant and reduce to standard pressure. But these reductions may be combined in one expression. If v denote the volume of a gas at $t°$ and p $^{mm.}$ of mercury, the reduced volume V may be found by means of the formula:

$$V = v\ \left(\frac{p}{760}\ \frac{273}{273 + t} \right)$$

or

$$V = v\ \left(\frac{273}{760}\ \frac{p}{273 + t} \right) [1]$$

---

[1] This formula is derived as follows:
By Boyle's Law,

$$v \infty \frac{1}{p},\ \text{where}\ T\ (\textit{absolute scale})\ \text{is constant};$$

Whence the rule:

*To reduce a given volume of gas to standard condi-
tions, multiply it by 273/760 (=0.359) and a fraction
whose numerator is the given pressure and whose denomi-
nator is the absolute temperature.*

NOTE. If the volume of a gas at a certain temperature and
pressure is to be found at any other temperature and pressure
than 0° and 760 *mm.*, only the fraction 273/760 needs to be
changed ; its numerator is made equal to the given absolute tem-
perature and its denominator to the given pressure.

Also sometimes the volume of a gas under standard conditions
is known and it is required to find the volume it occupies at a
certain stated temperature and pressure. In such cases the known
volume for V is substituted in the formula and the unknown
volume v calculated.

and by Charles' Law,

$$v \infty T, \text{ when } p \text{ is constant.}$$

Combining the two expressions,

$$v \infty \frac{T}{p}, \text{ or } \frac{vp}{T} = \text{a constant quantity.}$$

For an equal weight of the same gas under different conditions
of temperature, pressure, and volume, denoted by T', p', and v',
a similar expression is true:

$$\frac{v'p'}{T'} = \text{a constant quantity;}$$

and as the weight of the gas does not change, the constant quan-
tity is the same in both cases, so that

$$\frac{v'p'}{T'} = \frac{vp}{T}$$

and

$$v' = v \left(\frac{p}{p'} \frac{T'}{T} \right)$$

where if $v' (= V)$ denote the volume at 0° *C.* and 760 *mm.*, $T' =$
273, $p' = 760$, and $T = 273 + t$:

$$V = v \left(\frac{273}{760} \frac{p}{273 + t} \right)$$

MODES OF MEASURING GASES. A common mode of measuring the volume of a gas is the following: A graduated tube (Fig. 1), closed at one end, is filled with a liquid, usually water or mercury, closed with the thumb, a cork, or a glass plate, inverted and opened with its mouth below the surface of the liquid, which is contained in a vessel or dish commonly called a *pneumatic trough.* By means of a delivery tube the gas is then made to bubble up into the tube and displace the liquid. If the pneumatic trough is deep enough to permit of the tube being raised or lowered so that the level of the liquid inside and outside of the tube may be made the same, the pressure of the confined gas is equal to that of the atmosphere, as read from a barometer, and its volume is given by the reading on the tube at the level of the liquid. If the trough is not deep enough for this, the pressure of the enclosed gas

Fig. 1—GAS-MEASURING TUBE AND MERCURY PNEUMATIC TROUGH

The wires leading to the top of the tube connect with platinum wires fused in the glass. Such a tube is a eudiometer (§ 50)

will be less than that of the atmosphere, since the atmosphere has to support the column of liquid in the tube above the level of the liquid in the pneumatic trough.

Hence, to find the actual pressure exerted by the gas, the vertical distance between the surfaces of the liquid inside and outside of the tube is measured. If the liquid be mercury, this distance is subtracted from the barometric reading, and the remainder is the pressure of the gas. If any other liquid is used, the pressure of the column of liquid must be reduced to millimeters of mercury by multiplying it by a fraction whose numerator is its specific gravity and whose denominator is the specific gravity of mercury, both referred to water as standard. If h denote in millimeters of mercury the pressure of the column, the formula for the reduction of gas volumes becomes:

$$V' = v \left(\frac{273}{760} \frac{p-h}{273+t} \right)$$

VOLUME MEASUREMENTS BY MEANS OF WEIGHT MEASUREMENTS. The fact that one cubic centimeter of water weighs one gram[1] renders it possible to find volumes by means of weight measurements. Thus, if the volume of a gas, measured as just described, but with an ungraduated tube, be marked on the containing vessel with a rubber band, piece of gummed paper, etc., the weight of the water filling the inverted vessel up to this mark, if expressed in grams, may be taken as the volume of the gas in cubic centimeters.

28. Correction for Vapor Tension. When the liquid over which a gas is collected is somewhat volatile at the temperature of the measurement, a correction to the pressure has to be applied. Thus, a gas collected over water is permeated with water vapor, for water sends off vapor at all temperatures. This vapor, just like a gas, exerts a pressure or tension which opposes the pressure of the atmosphere as measured by the barometer and is greater

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[1] This is strictly true only at 4°. Its approximation to truth, however, is close enough for all purposes of our measurement of the volumes of gases at ordinary temperatures.

the higher the temperature. According to Dalton's Law:

·Each gas or vapor present in a mixture of gases or vapors exerts the same pressure as it would if it alone were present, or, in other words, *the pressure of a gaseous mixture is the sum of the partial pressures of its components.*

Hence, to find the pressure exerted by a gas alone, the pressure due to the vapor of the liquid must be subtracted from the total pressure of the gaseous mixture as given by reading of the barometer. The formula for reduction to standard conditions must then receive a further correction and reads, if p' denote the pressure of the vapor of the liquid:

$$V'' = v \left(\frac{273}{760} \frac{p-h-p'}{273 + t} \right)$$

The tension of water vapor as measured at ordinary temperatures is given in Table II. (See Appendix *D*.)

Problems

1. What is the volume at 760 *mm.* of mercury of 301.7 *c.c.* of a gas measured at 750 *mm.*?

Solution:

Calling the required volume v' we have :

$$\frac{301.7}{v'} = \frac{760}{750}$$

Whence,

$$v' = 301.7 \frac{750}{760} = 297.7 \ c.c.$$

2. What is the volume under standard pressure of :

(*a*) 728 *c.c.* of gas measured under 1,829 *mm.* of mercury ?

(*b*) 63 *l.* of gas measured under 378 *mm.* of mercury ?

(*c*) 28 *l.* of gas measured under 17.6 atmospheres ?

(*d*) 846 *c.c.* of gas measured under 0.738 atmospheres ?

3. What is the volume at 0° of 326 *c.c.* of gas measured at 22° ?
Solution :
Denoting the required volume by v'_1, we have :

$$\frac{326}{v'_1} = \frac{273 + 22}{273}$$

Whence, $\qquad v'_1 = 326\frac{273}{295} = 301.7\,^{c.c.}$

4. What is the volume at standard temperature of :

    (*a*) 935.6 *c.c.* of gas measured at 100°?

    (*b*) 26.4 *l.* of gas measured at — 10°?

    (*c*) 492.8 *l.* of gas measured at 84°?

    (*d*) 624.4 *c.c.* of gas measured at 62°?

5. What is the reduced volume of 256 *c.c.* of a gas measured at 660 *mm.* and 27°?
Solution :
Substituting in the general formula, we have :

$$V = 256 \left(\frac{273}{760} \frac{660}{273 + 27} \right) = 202.3 \ ^{c.c.}$$

6. What is the volume under standard conditions of 74 *l.* of gas measured at 950 *mm.* and 197°?

7. Reduce to standard conditions :

    (*a*) 14 *c.c.* of gas measured at 763 *mm.* and — 11°.

    (*b*) 6.2 *c.c.* of gas measured at 111 *mm.* and 27°.

    (*c*) 279 *c.c.* of gas measured at 725 *mm.* and 17°.

8. A vessel 20 *cm.* long, 10 *cm.* wide, and 5 *cm.* deep is filled with air at 790 *mm.* and 35°. What is the volume under standard conditions?

9. A gas volume measures 15.1 *c.c.* at 0° and 760 *mm.* What is its volume at 900 *mm.* and 17°?

10. If 654 *c.c.* of gas are measured at 16° and 734 *mm.*, what is the volume at 35° and 895 *mm.*?

11. The volume of a gas measured in a graduated tube over mercury was found to be 93 *c.c.*, the temperature being 17°, and the height of the barometer 738 *mm.* The level of the mercury inside the tube was 78 *mm.* higher than that in the trough. What would be the volume of the gas under standard conditions?
Solution :
Substituting in the formula, we have :

$$V' = 93 \left(\frac{273}{760} \frac{738 - 78}{273 + 17} \right) = 76.0 \ ^{c.c.}$$

12. A gas was measured over water (and hence was saturated with water vapor) at 20° and 744 *mm.*, and was found to have a volume of 628 *c.c.*, when the levels of the water inside and outside of the vessel were the same. What would its volume be under standard conditions?

Solution :

The tension of aqueous vapor at 20° is 17.4 *mm.* of mercury and substituting in the formula we have :

$$V'' = 628 \left(\frac{273}{760} \frac{744 - 17.4}{273 + 20} \right) = 559.4 \ c.c.$$

13. Reduce to standard conditions 937 *c.c.* of gas saturated with water vapor at 24° and 621 *mm.*

14. Reduce to standard conditions 76 *l.* of a gas saturated with water vapor at 21° and 763 *mm.*, when the difference of the water levels inside and outside the vessel containing the gas was 439 *mm.* (The specific gravity of mercury referred to water is 13.6.)

15. 146 *c.c.* of air at 23° and 746 *mm.* of mercury were measured over water. What volume would the dry gas occupy at 0° and 760 *mm.*?

16. If a certain mass of gas measures 300 *c.c.* when the barometer stands at 760 *mm.*, and later contracts to 297 *c.c.*, what is the barometer reading corresponding to the latter volume?

17. If a gas under standard conditions has its pressure doubled and its temperature raised until the volume is the same as its original volume, what is its final temperature?

18. What is the reduced volume of 77.7 *c.c.* of air saturated with water vapor, if measured at 17.5° with the barometer at 755.5 *mm.*, the aqueous tension being 14.9 *mm.*?

19. Reduce to standard conditions 1,328 *c.c.* of gas saturated with water vapor and measured under the following conditions : Pressure, 765 *mm.*; temperature, 18°; aqueous tension, 15.4 *mm.*

20. What volume under standard conditions would be occupied by 200 *c.c.* of gas at 14° and 756 *mm.*?

21. If a certain mass of air occupies 140 *c.c.* when the temperature is 27° and the height of the barometer 750 *mm.*, what will its volume be when the temperature is 9° and the barometer reading 770 *mm.*?

22. What is the volume of 1,520 *c.c.* of hydrogen measured at 54° with the barometer at 780 *mm.* if the temperature and barometer change to 18° and 740 *mm.*?

CHAPTER III

OXYGEN AND OZONE

OXYGEN

HISTORICAL NOTE. Oxygen was first isolated by the Englishman, Priestley, in 1774; also independently by the Swede, Scheele, a few months later. Its discovery attracted much attention. Lavoisier, in 1778, showed the important part it plays in the phenomena of combustion, and gave it the name of oxygen. Previous to that time it had been called *vital air, dephlogisticated air*, and the *eminently respirable air*.

29. Occurrence. Oxygen is the most abundant of all the elements. More than a fifth of the atmosphere consists of free or uncombined oxygen. In combination with other elements it forms nearly 50 per cent of the weight of the earth's crust. Water contains 88.81 per cent of it, and it is a constituent of most animal and vegetable substances.
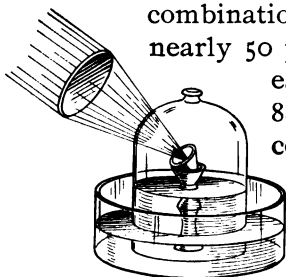
Fig. 2—APPARATUS FOR PREPARING OXYGEN BY FOCUSING THE SUN'S RAYS ON RED PRECIPITATE

30. Preparation. Although oxygen occurs uncombined in the atmosphere, it is difficult to free it from the other atmospheric gases, at least on a small scale. The usual way to prepare it is to heat certain of its compounds. Thus, mercuric oxid (red. precipitate), silver oxid, manganese dioxid (black oxid of manganese), potassium chlorate (chlorate of potash), and several other compounds

[26]
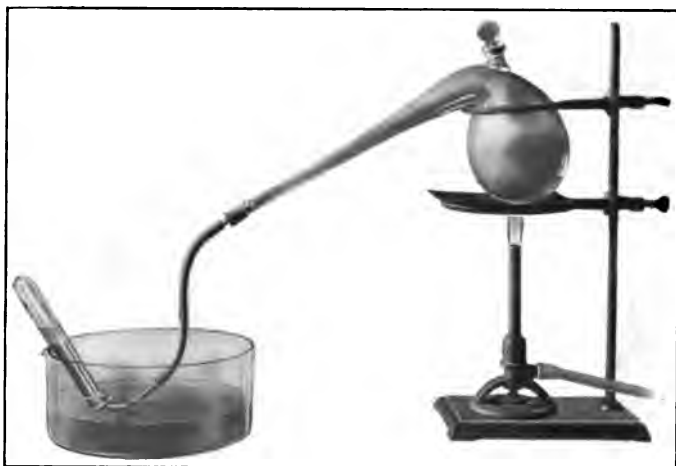
Fig. 3—PREPARATION OF OXYGEN BY HEATING A MIXTURE OF POTASSIUM CHLO-
RATE AND MANGANESE DIOXID IN A RETORT

yield oxygen when heated. Its preparation from red precipitate is historically interesting because Priestley first prepared the gas in a state of purity by using a lens to focus the sun's rays upon the compound. (Fig. 2.)

A mixture of potassium chlorate and manganese dioxid gives off oxygen much more readily when heated than does either of these compounds when heated alone. (Fig. 3.) While the potassium chlorate is thus converted into potassium chlorid and oxygen, the manganese dioxid does not seem to be at all changed. It helps along the reaction in some as yet unexplained way, without itself undergoing any permanent change.

CATALYSIS. There are numerous cases similar to this. Generally speaking, when the addition of a substance causes a reaction to take place between other substances, or alters the conditions of the reaction, as

its speed or the temperature at which it starts, and does not itself become permanently changed, such a substance is said to exercise a *catalytic action*, and the process is known as *catalysis*.

OTHER MODES OF PREPARATION. Oxygen may also be prepared by passing a current of electricity through a solution of copper sulfate, by the action of water on sodium peroxid, by the interaction of nitric acid, red lead, and potassium permanganate, by the action of cobalt nitrate on a mixture of bleaching powder and water, and by many other reactions. When liquid air evaporates, its oxygen, being less volatile, does not boil away as rapidly as the other main constituent, so that finally the liquid consists of over 90 per cent of oxygen, which is pure enough for many industrial purposes.

31. Properties. (Table I., Appendix *D*.) *Physical.* Oxygen is a colorless, odorless, and tasteless gas, but slightly soluble in water and other liquids. It is the most magnetic of all the gases. Liquid oxygen has a light blue color.

Chemical. It forms compounds with nearly all the elements. With some elements, notably phosphorus and potassium, union takes place at ordinary temperatures, but usually it is necessary to raise the temperature. The union of oxygen with other substances is commonly called *oxidation*, but when a substance combines with oxygen so as to give off light and heat, it is said *to burn*, and the process is called *burning* or *combustion*.

Combustible substances burn with much greater vigor in pure oxygen than in air. The reason for this is that the air contains about four times as much (by volume) of other gases, nitrogen, argon, etc., as it does of oxygen. Part of the heat of combustion is expended in raising the temperature of these gases, and, as the emission of light is greater

the higher the temperature, combustions in oxygen are much brighter than in air. When substances combine with oxygen without much, if any, manifestation of light and with but little change of temperature, the process is known as *slow combustion*.

32. Nomenclature. When oxygen combines with a single other element, the compound is called an *oxid;* thus, *mercuric oxid*, a compound of mercury and oxygen. The prefixes *di* and *bi* and *per* serve to distinguish the different oxids of the same element. Thus, manganese *dioxid* and sodium *peroxid* contain more oxygen than do manganese *oxid* and sodium *oxid*.

33. Oxidation and Reduction. Any substance containing oxygen which under suitable conditions can be transferred to another substance is called an *oxidizing agent*. The oxidizing agent is thereby more or less deprived of its oxygen and is said to be reduced. A *reducing agent* then is a substance that takes the oxygen from an oxidizing agent. Oxidation is the addition of oxygen; reduction is the subtraction of oxygen. When one substance is oxidized, another is always reduced.

DEFLAGRATION. As union between a combustible substance and an oxidizing agent can take place only where the two come in contact, the rapidity of combustion is increased by making the surface between the combustible and oxidizing agent greater. This can be accomplished by grinding them into powders and mixing them thoroughly. Oxidation may then be effected with great rapidity throughout the whole mixture. To such a sudden union of combustible and oxidizer is given the name of *deflagration*.

Gunpowder is a familiar example of such a deflagrating mixture; the oxidizing agent is saltpeter and

the reducing agents charcoal and sulfur. As the oxids of carbon and sulfur are gaseous, a large volume of gas is formed by the ignition of the powder, and if the powder be confined in the barrel of a gun, this sudden and enormous increase of volume calls forth a corresponding pressure; the result is that the bullet is shot out of the gun.

34. Uses. In a state of purity oxygen is used in producing the calcium light (§ 44) and in the treatment of lung diseases. As it occurs in the air it combines with combustibles, as coal, wood, etc., to furnish us with light, heat, and power. It is also indispensable in respiration, fermentation, and most kinds of decay.

OZONE

HISTORICAL NOTE. Van Marum in 1785 observed that during the working of a static electrical machine a peculiar odor was noticeable, and that mercury in the vicinity of the machine was tarnished. This "electrical smell" was investigated in 1840 by Schönbein, who proved that it was due to the presence of a new form of oxygen.

35. Allotropy. Ozone is but another form of oxygen. This is proved by the following facts:

1. Ozone can be completely transformed into ordinary oxygen.

2. A given weight of ozone yields an equal weight of ordinary oxygen.

3. Two volumes of ozone give three volumes of ordinary oxygen.

4. Three volumes of ordinary oxygen yield two of ozone.

There are then two varieties of the element oxygen. These are called *allotropic forms* or *allotropes*

of the element. A few other elements also may be obtained in allotropic modifications which often exhibit quite different chemical properties.

36. Occurrence. Ozone is found in the air in very small proportions, chiefly during and directly after thunder storms. It is formed by the action of the lightning on the oxygen in the air.
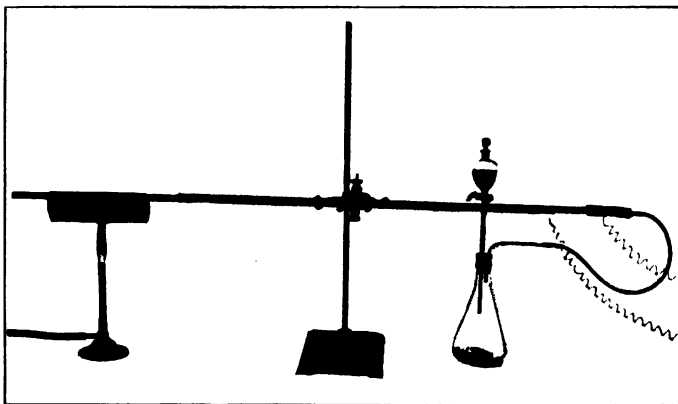
Fig. 4—A SIMPLE FORM OF OZONIZER

Ozonizers (Fig. 4) consist of two electrical conductors between which oxygen may be passed. The conductors are connected with an induction coil, and when the current is passed a multitude of tiny sparks strike through the oxygen, converting it in part into ozone. In the apparatus in the figure one conductor is a straight copper wire running through the tube, and the other is a wire coiled around the tube. To the right is an oxygen generator (by action of water on sodium peroxid). The left end of the tube is left bare and a roll of wire gauze slipped over it to spread the heat of a Bunsen flame used to decompose the ozone as it passes out of the tube.

37. Preparation. In most chemical reactions proceeding at low temperature and producing oxygen, ozone is also formed in small proportion.

If a stick of phosphorus be scraped clean and put into a bottle containing enough water to nearly cover it, ozone will soon be formed in the bottle. Also, if a red-hot glass rod be plunged into a flask filled with a mixture of air and ether vapor, ozone is produced. The best way to prepare ozone, however, is by the action of electrical discharges on oxygen in an apparatus called an "ozonizer."

38. Properties. *Physical.* Ozone is a colorless gas with a peculiar and irritating odor. When liquefied it is of an intensely blue color. It is quite soluble in turpentine, while oxygen is very slightly so. Hence ozone may be separated from oxygen by solution in that solvent.

Chemical. Ozone is totally decomposed into oxygen at temperatures above 20°. It is a most energetic oxidizing agent. It decomposes potassium iodid in solution, setting the iodin free, which, if brought in contact with starch, forms a blue compound.

Problems

1. Potassium chlorate when heated decomposes into oxygen and potassium chlorid. What is the per cent of potassium chlorid in the chlorate if 22 g. of the chlorate yield 8.62 g. of oxygen ?

2. If potassium chlorate contains 39.2 per cent of oxygen, how many grams of oxygen can be obtained from 20 g. of potassium chlorate ?

3. How many liters of oxygen under standard conditions can be obtained from 10 g. of potassium chlorate ?

4. How many liters of oxygen at 50° and 700 mm. pressure can be obtained from 10 g. of potassium chlorate, containing 10 per cent of potassium chlorid ?

5. How much oxygen was given off from how much potassium chlorate, if the residue of potassium chlorid amounted to 3.46 g.?

HYDROGEN

HISTORICAL NOTE. That acid liquors, when brought in contact with iron or zinc, effervesce and give off a "wind," was known at quite an early period, but the gas thus generated was supposed not to differ from atmospheric air. Cavendish, an Englishman, isolated the gas in 1776 and studied its properties, and Lavoisier gave it the name of hydrogen, *i. e.*, *water producer*, because the sole product of its combustion is water.

39. Occurrence. Hydrogen occurs free in small proportions in the extreme upper regions of the atmosphere of the earth, and in some volcano gases, but is present in enormous quantities in the sun's atmosphere. It forms 11.19 per cent of the weight of water and is a constituent of most animal and vegetable substances.

40. Preparation. A current of electricity passed through water decomposes it into hydrogen and oxygen. At high temperatures water dissociates (page 60) into oxygen and hydrogen, and if some substance, as iron, is present, this will unite with the oxygen to form a solid compound, the hydrogen going free. By passing steam over very hot iron, then, hydrogen may be prepared. The alkali metals (page 183) and the alkalin earth metals (page 251) react with water, setting half of its hydrogen free and forming *hydroxids* of the respective metals, which dissolve in the excess of water present. The hydrogen of these hydroxids can be expelled by

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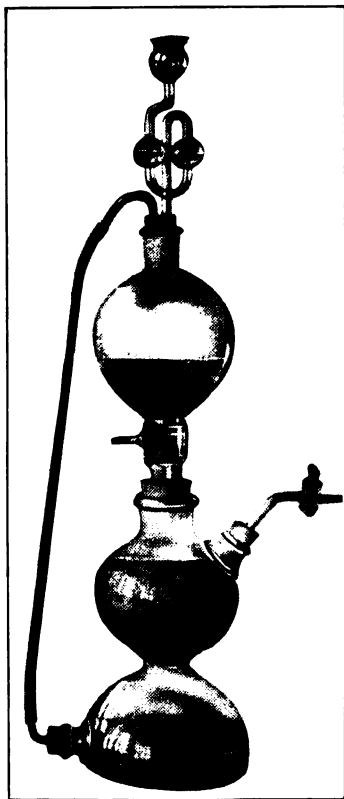
Fig. 5—KIPP'S GAS GENERATOR

the action of aluminum or zinc on their solutions, or by heating the solid hydroxids with powdered iron or zinc. Acids when acted upon by certain metals, especially magnesium, zinc, and iron, yield hydrogen. Zinc and dilute sulfuric or hydrochloric acids are usually used.

Kipp's gas generator (Fig. 5) is a convenient apparatus for supplying hydrogen at any time. The solid (zinc) is placed in the middle globe and the liquid (dilute sulfuric acid) in the upper. By opening the stopcock between the upper and the middle globes, the acid flows down upon the zinc, and the gas generated escapes through the stopcock delivery tube at the right. If this stopcock is closed, the gas, having no outlet, comes under a greater and greater pressure, and the liquid which has run through the solid into the lowest compartment is finally forced up through the rubber tube at the left, into the upper globe, the excess of the gas escaping through the funnel tube.

41. Physical Properties. (Table I., Appendix *D*.) Hydrogen is a colorless, odorless, and tasteless gas, but slightly soluble in water and other liquids; it is the lightest known substance.

DIFFUSION; TRANSPIRATION. Hydrogen is characterized by the rapidity with which it mixes with other gases (*diffusion*) and the ease with which it passes through porous plates of plaster of paris, plumbago, etc., and narrow tubes (*transpiration*). Graham, who made a study of the transpiration of gases, discovered the following law:

The weights of gases taking equal times to pass through the same porous plate under similar conditions are inversely proportional to the square roots of their specific gravities.

Thus, the specific gravity of oxygen referred to hydrogen is 16; hence hydrogen traverses porous plates four times as fast as does oxygen.

42. Chemical Properties. Hydrogen burns in the air with an extremely hot and almost invisible flame; in oxygen its combustion is much more vigorous. Under certain conditions it can unite with oxygen already in combination with other elements. Thus, when lead or copper is heated in contact with oxygen, oxids of lead or copper are formed. If these oxids are heated in an atmosphere of hydrogen, the oxygen leaves the metals and unites with the hydrogen, forming water. Hydrogen may thus act as a reducing agent (§ 33).

LIQUID HYDROGEN. Liquid hydrogen is colorless, has a clearly defined surface, drops well, and can be poured from one vessel to another. It is a non-conductor of electricity and is very slightly magnetic. It is the lightest known liquid, being only one-fourteenth as heavy as water. It is the coldest liquid known, boiling under ordinary pressure at 20.5° absolute, and it may be solidified into a clear, transparent ice.

43. Nascent State. While hydrogen does not react with most other elements except at temperatures somewhat above 500°, yet, at the moment of its formation, when it is said to be in the *nascent*

state, it brings about reactions even at ordinary temperatures. Similarly, oxygen, the moment it is set free from combination acts more powerfully than afterward. The great oxidizing power of ozone is perhaps due to nascent oxygen, ozone breaking up into oxygen.

44. Uses. Hydrogen is used to inflate balloons, but is especially employed in attaining high temperatures by its combustion in oxygen, whereby a temperature of nearly 2,800° may be reached. In the production of this high temperature, great care

Fig. 6—SECTIONAL VIEW OF AN OXYHYDROGEN BLOWPIPE

must be taken to prevent the mixing of the gases before they are burned, else most serious explosions may result. A burner of the form shown in Fig. 6 may be safely used. This consists of an outer tube, drawn down to a tip at one extremity and furnished with a stopcock at the other. In the axis of this tube is a second similar tube, which can be moved to and fro. The hydrogen is fed into the outer tube and the oxygen through the inner; their proportions and the relative positions of the tips are adjusted until the flame is thin and straight. All danger of explosion is avoided by the use of such a burner, for the gases do not mix except at the moment of combination. If the *oxyhydrogen flame*, as that produced by the burning of hydrogen is called, is directed against a piece of lime, this is heated to incandescence and gives out a very brilliant light (calcium light).

Exercises

1. What familiar compounds contain hydrogen?

2. To what is the danger of an explosion with hydrogen due, and how may it be avoided?

3. What property of hydrogen makes it useful for inflating balloons? What property makes it rather disadvantageous?

4. What property of hydrogen may best serve as its test?

Problems

1. The specific gravity of ozone is 24, and that of oxygen is 16. What is the ratio of their speeds of transpiration?

2. The specific gravity of chlorin is nearly 36. Compare its speed of transpiration with that of hydrogen.

3. A certain gas passes through a porous plate 3.8 times slower than does hydrogen. What is its specific gravity?

4. Oxygen and hydrogen are separated by a porous partition, and 3.84 *c.c.* of hydrogen pass through in one second. What volume of oxygen passes through in the same time in the opposite direction?

5. One liter of hydrogen weighs 0.09 *g.* and one liter of oxygen 1.43 *g.* What is the specific gravity of hydrogen referred to oxygen as a standard? Of oxygen referred to hydrogen?

6. What is the volume in liters of 2 *g.* of hydrogen? Of 32 *g.* of oxygen?

7. A balloon of 500 cubic meters capacity is to be filled with hydrogen at 20° and 800 *mm.* pressure. What will be the weight of the hydrogen?

8. If hydrogen chlorid contains 2.7 per cent of hydrogen, how many liters of hydrogen at 93° and 265 *mm.* can be obtained from 38 *g.* of the chlorid?

9. If water contains 11.19 per cent of hydrogen, how many liters of hydrogen at 16° and 743 *mm.* can be obtained from one kilogram of water?

10. If 23 *g.* of sodium liberate one gram of hydrogen from water, how many grams of the metal must be employed to prepare 100 *l.* of the gas at 22° and 752 *mm.*?

11. What is the weight of a liter of hydrogen collected over water at 50° and 743 *mm.*? (See problem 5 for data.)

12. Under standard conditions what would be the volume of the gas considered in the last problem?

THE COMPOUNDS OF OXYGEN AND HYDROGEN

There are two compounds of oxygen and hydrogen, or oxids of hydrogen — hydrogen monoxid (water) and hydrogen dioxid (peroxid).

WATER

HISTORICAL NOTE. Water was supposed to be an element (page 9) until Cavendish in 1781 showed that it was produced by the burning of hydrogen.

45. Occurrence. Water is found in the atmosphere in the form of invisible vapor which may condense into mist, fog, or cloud, and these may fall to the earth as rain, hail, or snow. The rain or melted snow and hail soak into the ground and collect in springs, rivers, lakes, oceans, etc. The differences in these "natural waters" are due to the dissolved substances they contain. Nearly all vegetable and animal substances contain more or less water which escapes when they are heated or otherwise dried.

THE "NATURAL WATERS." *Rain water* is nearly pure water, containing only the impurities which were present in the air through which it fell. The commonest of these impurities are ammonia, nitric acid, and saline, vegetable and animal substances.

Spring water is rain water which has soaked into the ground. The water descends until it comes to an impervious stratum, along which it flows to collect in some hollow, or to issue at the surface of the earth, often

many miles from where it entered. Spring waters hold in solution various substances, depending upon the nature of the ground over which they pass. *Mineral waters* are spring waters containing certain substances of peculiar taste, many of which are reputed to be of medicinal value. They may be classed into : *Saline waters*, containing common salt ; *alkalin waters*, containing common soda ; *bitter waters*, containing magnesium compounds ; *chalybeate waters*, containing iron compounds ; *aërated waters*, containing carbonic acid gas ; *sulfur waters*, containing hydrogen sulfid.

River water is derived from rain and spring water. The substances held in suspension or solution by it depend upon the nature of the river bed as well as of the waters flowing into it.

Sea water is chiefly concentrated river water. The dissolved substances contained in the waters of the rivers discharging into the sea or ocean are mostly non-volatile, and hence are left behind when the sea water evaporates. The vapor is very often carried far inland, only to be precipitated to flow back again into the sea. This perpetual washing out or leaching of the soil results in a continually increasing proportion of soluble matter in the sea, and it may be truly said that the sea contains, in minute traces, at least, every soluble substance on the earth. Common salt is the main dissolved substance in sea water. The water of inland bodies of water without any outlet, as the Great Salt Lake in Utah, is also salty.

46. Distillation. The process known as distillation consists in converting a liquid into vapor, separating the vapor from the liquid, and then condensing it. The apparatus consists of a part to vaporize the liquid, usually called a *still*, and a part to condense the vapor, sometimes called a *worm* and sometimes a *condenser*. The liquid is boiled in the still *S* (Fig. 7), its vapor passing into the coiled, wormlike tube *W*, around which cold water is made to circulate.

A form in common use in laboratories (Fig. 8) consists of a flask connected by means of a curved tube and corks, with a condensing apparatus called a *Liebig's condenser*. This is simply a straight tube running through the axis of a larger but shorter tube through which a current of cold water is made to pass.

Substances which are practically involatile at ordinary temperatures may be separated from the liquids with which they are mixed by distillation. The separation of a mixture of volatile substances, as water and alcohol, by means of distillation, is but partial, the distillate always containing some of all the substances, the more volatile in the greater proportion.

Fig. 7—STILL AND CONDENSER

47. Filtration. The process of passing a liquid impregnated with or holding in suspension solid particles, through some porous material, as paper, cloth, sand, charcoal, etc., is known as filtration. If the pores be small enough, all the solid matter may be removed. It is hard, however, to prepare

filters with fine enough pores to remove bacteria, etc., from water, although some kinds of baked clay succeed fairly well.
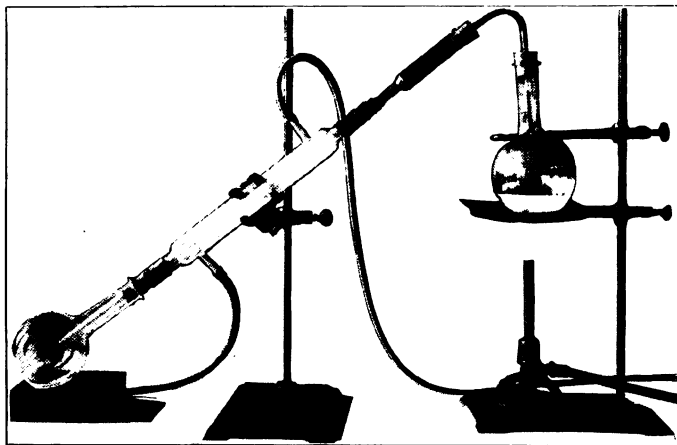
Fig. 8—APPARATUS FOR DISTILLING SMALL QUANTITIES OF LIQUID

FILTRATE-AND PRECIPITATE. The liquid which passes through is called a *filtrate*. When on mixing one liquid with another, an insoluble solid is formed, this is said to be precipitated and is known as a *precipitate*.

PURIFICATION OF DRINKING WATER BY FILTRATION. Wholesome drinking or potable water should be clear, free from disease germs, and should not contain too much mineral matter in solution, although a little does no harm. A source of pure water is not available in some cities; hence recourse must be had to purifying processes. Boiling the water kills the germs, but is too expensive for use on a large scale. *Coagulation filters* and *intermittent sand filters*, or the two combined, have proved successful in many cases. Fine particles of clay, etc., may remain suspended in water for a long time, but if minute proportions of certain substances, as alum, etc., be added, the particles flock together and settle much more rapidly. A considerable proportion of the disease germs clings to these particles and is

thus separated from the water. Subsequent filtration through coke dust and sand removes the coagulated particles, together with the germs adhering to them.

In the intermittent process, beds of sand several acres in extent are prepared, the upper layers consisting of fine, the lower of coarse sand. Tile drains are set in the lower layers to collect and conduct to a reservoir the purified water that filters through. These beds are flooded with water which is treated with some coagulating agent. After the water soaks through, the sand is allowed to dry and flooding is repeated.

The *taste* and *wholesomeness* of water also depend to some extent upon the dissolved gases it contains. Water deprived of its dissolved gases by boiling tastes flat; its taste may be improved by shaking it up with air.

48. Formation. Water is formed in all the phenomena of nature in which hydrogen is oxidized. As wood and similar combustibles contain hydrogen, water is produced when they burn. Also, as hydrogen is a constituent of most animal and vegetable substances, water is formed when they putrefy and decay.

49. Preparation. The combustion of hydrogen or of substances containing hydrogen yields water. Hydrogen starts to burn only when heated to temperatures above 600°. At ordinary temperatures, mixtures of hydrogen and oxygen may be preserved indefinitely without any appreciable combination occurring. The same is true of the chemical union of many other substances.

As a rule, low temperatures tend to prevent reaction, while high temperatures aid it. If one portion of a mixture of hydrogen and oxygen be heated to the combining temperature, union ensues with evolution of enough heat to bring the neighboring portions up to the combining temperature

so that they unite also. Union of the whole mixture is thus rapidly effected, and the speed with which the union spreads through the mixture has been found to be 2,810 meters per second.

50. The Volumetric Composition of Water by Eudiometric Measurements. The instrument generally employed to show the union of measured volumes of gases is the eudiometer. One of the simplest forms consists of a straight tube 60 to 80 *cm.* long, in the closed end of which are sealed two platinum wires with their inner extremities quite close together. The eudiometer is filled with mercury and inverted in a mercury pneumatic trough. (Fig. 9.)
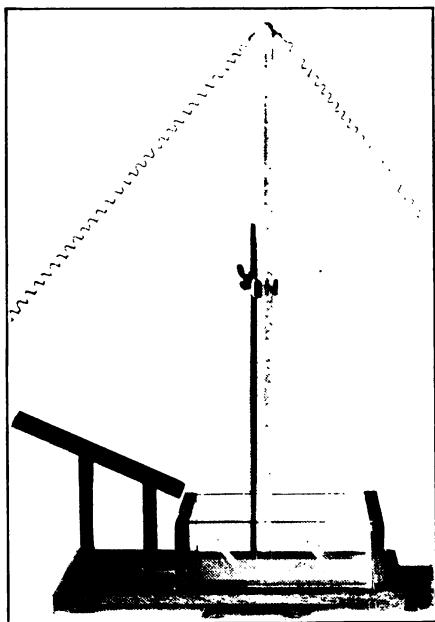
Fig. 9—EUDIOMETER AND MERCURY PNEUMATIC TROUGH

The sides of the trough are of plate glass so that the level of the mercury may be accurately seen. The slanting support at the left is used to lay the eudiometer on when a gas is introduced

Some dry hydrogen is made to pass up the tube to expel some of the mercury. The volume of the gas added is read and reduced to standard conditions of temperature and pressure (§ 27). A volume of
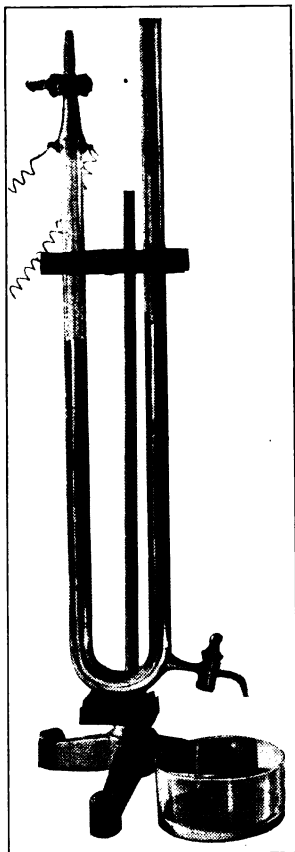
Fig. 10—ANOTHER FORM OF
EUDIOMETER

*By bending it around so as to form
a U tube, the second branch acts as
a pneumatic trough*

dry oxygen a little larger than that of the hydrogen is then introduced, measured and reduced to standard conditions. (Fig. 10.)

To start the reaction, the outer extremities of the platinum wires are connected to the terminals of an induction coil and the circuit closed. The electric sparks between the wires heat the mixture in their vicinity to the combining temperature, and all the hydrogen burns with almost explosive violence. The volume of the water produced is so small in comparison with the volumes of the gases that it may without appreciable error be neglected. The volume of the residual oxygen is measured, reduced to standard conditions, and subtracted from the volume of oxygen taken at first. This difference is the volume of oxygen combining with the volume of hydrogen taken. The ratio of these volumes is found to be 1 : 2. One volume of oxygen combines with two volumes of hydrogen. If the

experiment be conducted at temperatures above 100°, so that the water formed vaporizes, and the volume of the steam be measured, its reduced volume will be found to equal that of the hydrogen.

Two volumes of hydrogen unite with one volume of oxygen to give two volumes of water vapor.

51. Volumetric Laws of Chemical Combination. The experiment just described has been repeated many times, always with the same result. Two facts taught by it are of fundamental importance:

1. The same volume of water vapor always results from the union of the same volumes of oxygen and hydrogen. There is a fixity, a definiteness in the proportions of the volumes. This definiteness has been found in the combination of all gases, although the proportion may vary from case to case. These facts are summed up in the Law of Definite Proportions by Volume:

The same volumes of reacting gases always produce the same volumes of gaseous compounds.

2. Two volumes of water vapor are produced by the union of two volumes of hydrogen and one volume of oxygen; the volumes of the gases are in the ratio 2 : 2 : 1. What is striking in this fact is that the ratio is expressible by *small, whole* numbers. It is certainly remarkable that of all conceivable ratios such simple, integral ones should be found. Other gases behave similarly, although the ratios may be different, and the facts find their general expression in the Law of Volumetric Proportions:

The volumes of reacting gases stand in a simple, integral ratio to one another and to the volumes of the gases produced.

52. Law of Definite Proportions by Mass or Weight. One liter each of hydrogen, oxygen, and water vapor weighs 0.09^g, 1.43^g, and 0.805^g, respectively. The ratio of these numbers is nearly 1 : 16 : 9. (To avoid overtaxing the memory with decimals, these numbers are rounded off to the nearest integers.) Now, 2^l of hydrogen combine with 1^l of oxygen to give 2^l of water vapor. Hence, 2 × 0.09 (= 0.18)^g of hydrogen unite with 1.43^g of oxygen to give 2 × 0.805 (= 1.61)^g of water vapor, or, rounding off to the nearest integers, one part of hydrogen combines with eight parts of oxygen to produce nine parts of water.

We may arrive at the same conclusion by a slightly different way. The specific gravities (referred to hydrogen) of water vapor and of oxygen are 9 and 16, respectively. Then two volumes of water vapor and one volume of oxygen weigh, respectively, 9 and 8 times as much as two volumes of hydrogen. Hence, as these are the volumes required in the reaction of hydrogen and oxygen to produce water, nine parts of water are produced by the union of eight parts of oxygen with one part of hydrogen.

Innumerable experiments have shown that this is always true of water: the ratios of combination by mass or weight are fixed and invariable. Similar conclusions have been arrived at for every other definite compound. All such facts find their general expression in the Law of Definite Proportions by Mass or Weight:

A definite compound always contains the same constituents united in the same proportions by mass or weight.

53. Composition of Water by Gravimetric Measurements. The proportions in which oxygen and hydrogen unite to form water can also be ascertained by operations involving determinations of weight alone. When copper is heated in the air, it combines with oxygen and forms the black oxid of copper. This when heated in hydrogen loses
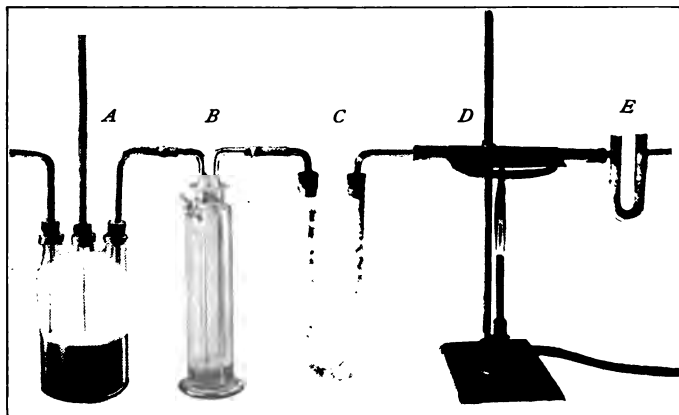
Fig. 11—APPARATUS FOR SHOWING THE COMPOSITION OF WATER
GRAVIMETRICALLY

its oxygen which unites with hydrogen to form water, and the copper oxid is thus reduced (§ 42). The water can be collected by passing its vapor over some substance, as calcium chlorid, which will absorb it. The apparatus (Fig. 11) consists of a hydrogen generator, a wash bottle, *A*, partially filled with potassium permanganate solution, a wash cylinder, *B*, containing some strong sulfuric acid, a U-tube, *C*, filled with calcium chlorid, a hard glass tube, *D*, about 20 $^{cm.}$ long and 1 $^{cm.}$ in bore, and a second chlorid of calcium tube, *E*,

serving to retain the water formed. The potassium permanganate solution removes certain impurities from the hydrogen, while the sulfuric acid and calcium chlorid dry it.

The hard glass tube is thoroughly dried, the middle part nearly filled with dry copper oxid and carefully weighed. The second chlorid of calcium tube, E, is also weighed. The apparatus is then put together as shown, and hydrogen passed through it. As soon as the hydrogen has driven out all of the air, the portion of the tube underneath the oxid is heated nearly to redness. When the black color of the oxid has changed to red, the reduction is complete. The heating is then discontinued and the current of hydrogen kept passing until the tube is cool. The tube and copper, and the chlorid of calcium tube are again weighed. The loss of weight of the former is equal to the weight of the oxygen given up by the copper oxid, and the increase in the weight of the latter is the weight of the water formed.

The difference between the weights of the water and of the oxygen is the weight of the hydrogen used. The weights of the hydrogen and oxygen required to produce the weight of water formed have thus been found. For example, Berzelius and Dulong, who in 1820 originated this experiment, found the loss in weight of the tube containing the copper oxid to be 27.129 ^{g}, and the gain in weight of the chlorid of calcium tube to be 30.519 ^{g}, *i. e.*, 30.519 ^{g} of water were formed containing 27.129 ^{g} of oxygen. Hence, 3.390 ^{g} (the difference between 30.519 and 27.129) of hydrogen must have combined with 27.129 ^{g} of oxygen to produce 30.519 ^{g} of water.

The ratio of these numbers — 3.390 : 27.129 : 30.519 — is approximately the same as 1 : 8 : 9 or 11.19 : 88.81 : 100.

54. Relations Between the Laws of Definite Proportions. Water then consists of 88.81 per cent of oxygen and 11.19 per cent of hydrogen. Now as 0.805 $g.$ of water vapor, 0.09 $g.$ of hydrogen, and 1.43 $g.$ of oxygen, each occupy the space of one liter, 100 $g.$ of water vapor occupy 100/0.805 = 124 $l.$ (rounding off to the nearest integer), 88.81 $g.$ of oxygen occupy 88.81/1.43 = 62 $l.$, and 11.19 $g.$ of hydrogen occupy 11.19/0.09 = 124 $l.$. The ratio of these numbers — 124 : 62 : 124 — is the same as 2 : 1 : 2, just as has already been directly found. In Berzelius and Dulong's determination, the 3.390 $g.$ of hydrogen occupied 3.390/0.09 = 38 $l.$, the 27.129 $g.$ of oxygen, 27.129/1.43 = 19 $l.$, the 30.519 $g.$ of water vapor, 30.519/0.805 = 38 $l.$, and these volumes are again seen to be in the ratio of 2 : 1 : 2.

Knowing then the percentage composition of water and the weights of equal volumes of hydrogen, oxygen, and water vapor, we can compute the volumes of the gases entering into and produced by the reaction yielding water. From the Law of Definite Proportions by Mass we can pass to that of Definite Proportions by Volume. We have already (§ 52) learned how to pass from the Law of Definite Proportions by Volume to that of Definite Proportions by Mass. The laws are thus seen to be identical in essence. Attention has already (§ 14) been directed to the invariable composition which is one of the items that distinguishes a mixture from a compound.

5

55. Law of Conservation of Matter (Persistence of Mass). Eight parts of oxygen combine with one part of hydrogen to produce nine parts of water; the sum of the weights of the hydrogen and oxygen is equal to the weight of the water.
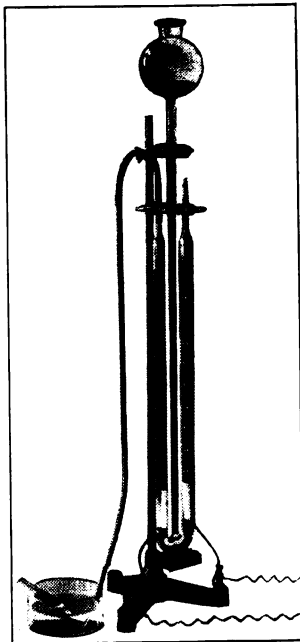
Fig. 12—VOLTAMETER
Lecture-table form

Like results have been found to be true of all reactions:

The sum of the masses of the reacting substances or factors *is equal to the sum of the masses of the substances produced or* products.

But this is the Law of Conservation of Matter (§ 15).

56. Synthesis and Analysis. By burning hydrogen in oxygen we have effected the synthesis of water, *i. e.*, we have put hydrogen and oxygen together in proper proportions and under suitable conditions and have obtained water. Its synthesis was also effected by bringing hydrogen into contact with hot copper oxid, which itself was decomposed into copper and oxygen. In the first case, account was taken of the volumes; in the second, of the weights. The opposite of synthesis is analysis, and we now proceed to ascertain the composition of water analytically.

57. Analysis of Water. Water may be decomposed into its elements by passing a current of electricity through it. As water itself is a very poor conductor of electricity, a small proportion of an acid or alkali is added to increase its conductance. The instruments employed are called *voltameters*, and consist essentially of two electrodes or places for the entrance and exit of the electric current, and two graduated tubes to collect the gas rising from the electrodes (Figs. 12 and 13). The electrodes are immersed in the liquid, the tubes filled with the same and inverted over the electrodes. As the current passes, gases arise from the electrodes and displace the liquid in the tubes. An examination of these gases shows that one

Fig. 13—ANOTHER FORM OF VOLTAMETER

is hydrogen and the other oxygen; the volume of the hydrogen is twice that of the oxygen.

Water is thus decomposed into two volumes of hydrogen and one of oxygen. If the liquid be weighed before and after passing the current, and the weights of the gases ascertained, it will be found that the loss in weight of the former is equal to the weights of the latter, and that the ratio of these weights is 9 : 8 : 1. If both the gases be caught in the same receiver (Fig. 14) and then transferred to an eudiometer and exploded, it will be found that if the experiment be carried out at temperatures above 100°, three volumes of the mixture will contract to two volumes of a gas which proves to

be water vapor. Now since there were two volumes of hydrogen to one of oxygen, we again see that two volumes of hydrogen combine with one volume of oxygen to yield two volumes of water vapor.

Fig. 14—APPARATUS FOR COLLECTING IN THE SAME RECEIVER THE HYDROGEN AND OXYGEN FROM THE ELECTROLYSIS OF WATER

The electrodes are of nickel or iron and the water has a little sodium hydroxid in it. The gases collecting just below the stopper can, by means of the delivery tube, be collected in any convenient receiver by water displacement

58. Chemical Equations. The Law of Definite Proportions affirms that fixed relative amounts of hydrogen and oxygen react to produce water, and the Law of Persistence of Mass that the sum of the masses of the factors must equal the sum of the masses of the products. The sign of equality may be used to show that this latter law holds good in a reaction, and the reaction under discussion may be expressed in the form of an equation. Thus, when the reacting masses are expressed in percentages, we have:

11.19% *hydrogen* + 88.81% *oxygen* = 100% *water*,

or, expressing them as the weights of the number of liters reacting:

0.18 *g. hydrogen* + 1.43 *g. oxygen* = 1.61 *g. water vapor*,

or, as parts by weight:

One part *hydrogen* + eight parts *oxygen* = nine parts *water*.

It is customary to write the factors of an equation to the left and the products to the right of the equality sign. "Shorthand methods" of expressing factors and products will be given later.

An equation merely expresses the fact of the equality of the masses of the factors and the products. It gives no information as to the nature of a reaction, and it does not tell why it takes place, or what are the causes for it. It is particularly to be noted that a chemical equation does not denote an equality of volumes. In the reaction between oxygen and hydrogen the volume of the product (water) is but two-thirds that of the factors. There is no law of conservation of volumes, and in a compound the elements are, so to speak, more crowded together than in the uncombined state.

59. Physical Properties. Water is an odorless, tasteless liquid. It is transparent and colorless when viewed in small quantities, but in large amounts it presents a deep blue or a green color. It is so common that its gaseous and solid states have received the special names of *steam* and *ice*. Like all other pure liquids, it freezes at a definite temperature, which is taken as one of the fixed points in graduating thermometers (§ 19). Its freezing point is but slightly affected by change of pressure, but its boiling point depends largely upon the pressure.

At 0° water has a vapor tension (§ 28) equal to 4.57 $^{mm.}$ of mercury. As the temperature rises the vapor tension increases at a more and more rapid rate, until at 100° it amounts to 760 $^{mm.}$ of mercury; *i. e.*, at the boiling point the tension

equals the pressure of the atmosphere. It is necessary, therefore, in giving the boiling point of a liquid, to specify the pressure. Pure water is a very poor conductor of heat and electricity.

60. Solution. A substance is said to dissolve when, on being brought in contact with a liquid, a homogeneous mixture is formed. The liquid is called the *solvent;* the substance which dissolves in it, the *solute.* Solution is hastened (1) by using solids in condition of powder, (2) by agitation so as to bring fresh surfaces of solute and solvent in contact, and (3) usually by raising the temperature. The amount of a solute which will dissolve in a given amount of the solvent depends mainly upon its nature and upon the temperature; crystalline form and pressure also have some slight influence. When a solvent refuses to dissolve any more of a substance with which it is in contact at a certain temperature, the solution is said to be saturated.

A saturated solution presents a case of equilibrium between the relative amounts of solvent and solute. If the conditions determining the equilibrium, as the temperature and crystalline form, be changed, the *solubility*, or the amount of a solute with which a definite amount of a solvent becomes saturated, is correspondingly changed. As a rule, the solubility of most solids and liquids increases with rise of temperature, although exceptions are not uncommon. The solubility of gases, however, always decreases with rise of temperature. Solubilities are usually given as the per cent of the solute in the solution saturated at a stated temperature.

61. Supersaturation. If a saturated solution of a solid more soluble in a solvent when hot than when cold be prepared at a higher temperature, separated perfectly from the solid (by decantation or filtration), and then slowly and quietly cooled to a lower temperature, the cooled solution may contain more of the solute than is required for saturation at the lower temperature. The solution is in that case said to be *supersaturated.* If a fragment, no matter how minute, of the solid solute be added to the solution, the excess soon crystallizes out. Sometimes even a jarring of the vessel containing the solution will bring about the same result. Analogous statements are true of gases. Addition of other substances will not relieve the condition of supersaturation unless they have the same crystalline form as the solute.

62. Water of Crystallization. Water enters into combination in fixed proportions with many substances, forming crystalline compounds. The union is but loose, for the water may be expelled from crystals by removing the water vapor from the adjoining space or by heating the crystals whereby the tension of the vapor of the water of crystallization is increased. This combined water is called *water of crystallization.* " Burnt alum," for instance, is nothing but ordinary alum deprived of its water of crystallization by heating.

NOTE. When crystals are formed from solution they sometimes enclose in little cavities some of the liquid (often called "mother liquor"). When crystals containing such *mechanically enclosed water* are heated the water vaporizes and the steam finally exerts enough pressure to suddenly break the crystal apart ; its fragments are often thrown some distance.

63. Efflorescence and Deliquescence. When some substances containing water of crystallization are exposed to a free circulation of dry air they lose this "crystal water" and usually fall away into a powder. Such substances are said to *effloresce*. Certain other substances, on the contrary, when exposed to the air, take up water vapor from it, and may absorb enough to form a solution; they are said to *deliquesce*.

HYDROGEN DIOXID

64. Preparation. Cold dilute acids act upon metallic peroxids with formation of hydrogen dioxid. To prepare this substance in a state of purity, dilute sulfuric acid and barium peroxid are used, as the barium sulfate which is also formed is insoluble in water, and may be separated from the solution of the hydrogen dioxid by filtration. The solution is allowed to stand over strong sulfuric acid, which absorbs the water as it evaporates, and by cooling to a low temperature, the hydrogen dioxid may be made to crystallize.

65. Properties. *Physical.* Pure hydrogen dioxid forms colorless crystals which a little water converts into a liquid of syrupy consistence and an unpleasant "metallic" taste. It mixes in all proportions with water.

Chemical. Hydrogen dioxid decomposes into water and oxygen at temperatures above 20°. Very dilute solutions, however, are quite stable. The ease with which it yields oxygen makes it a good oxidizing agent. Under certain circumstances it may also act as a reducing agent.

66. Uses. In dilute solution hydrogen dioxid is employed in bleaching hair, silk, wool, feathers, bone, and ivory; as an antiseptic in surgery, and as a toothwash in dentistry; also as a preservative for milk, beer, wine, and other fermentable liquids. Artists use it to renovate old paintings.

COMPOSITION. As hydrogen dioxid cannot be prepared by the direct union of its elements, its composition cannot be directly determined by synthesis. This has been fixed by analysis, however, as follows: When heated it breaks up into a mixture of two volumes of water vapor and one of oxygen. Now, two volumes of water vapor contain two volumes of hydrogen and one of oxygen. Hence, hydrogen dioxid consists of equal volumes of oxygen and hydrogen. Furthermore, the gravimetric analysis of hydrogen dioxid proves it to contain sixteen parts of oxygen to one part of hydrogen.

67. Law of Multiple Proportions. Hydrogen and oxygen form two compounds. Many other elements also unite in two or even more proportions to form perfectly distinct compounds. For all such cases the Law of Multiple Proportions is true; it may be stated as follows:

If two or more elements unite to form two or more compounds, the amounts (expressed either by weight or by volume) of the element or elements that unite with a fixed amount of one element stand in an integral (and usually simple) relation to one another.

Thus, one part by weight of hydrogen combines with eight parts of oxygen to form water, and with sixteen parts of oxygen to form hydrogen dioxid, and the ratio of 8 : 16 is the same as 1 : 2. Also two volumes of hydrogen combine with one volume of oxygen to form water, and with two volumes of

oxygen to form hydrogen dioxid; and here again the ratio is very simple. Strictly speaking, there are two Laws of Multiple Proportions, one having reference to mass or weight and the other to volume. The former is always applicable, the latter only when the substances are vaporizable. There can, however, be but slight objections to combining them, as by so doing their similarity is perhaps rendered the more evident.

THERMOCHEMISTRY

EXPLANATION OF TERMS. When substances combine chemically, heat is always liberated or absorbed; the products become warmer or colder than the factors. The branch of science that treats of these changes is called *Thermochemistry, i. e., Heat-chemistry*. Descriptive chemistry concerns itself chiefly with changes in matter; thermo-chemistry with changes in heat and chemical energy. The unit of heat, called a *calory*, is the amount of heat required to change the temperature of one gram of water one degree.

EXOTHERMIC AND ENDOTHERMIC REACTIONS. If heat be evolved in a reaction, it is said to be *exothermic*, while if heat be absorbed it is *endothermic*. When 2 g. of hydrogen unite with 16 g. of oxygen to form 18 g. of water, 68,400 calories of heat are set free; the reaction is exothermic. To decompose 18 g. of water into its elements requires the expenditure of exactly the same amount of heat energy; the decomposition of water is an endothermic reaction. These facts may be expressed in the form of equations as follows:

2 g. *hydrogen* + 16 g. *oxygen* = 18 g. *water* + 68,400 calories.
    (reacts with)   (to give)   (with an evolution of)

or,

18 g. *water* = 2 g. *hydrogen* + 16 g. *oxygen* — 68,400 calories.
    (decomposes into)   (and)   (with an absorption of)
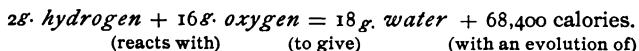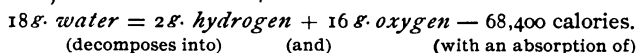
Hydrogen and oxygen do not combine directly to form hydrogen dioxid so as to enable the heat change

to be measured, but the compound once prepared can easily be decomposed into its elements and the heat determined. The decomposition of 34 *g.* of hydrogen dioxid is accompanied with the evolution of 232 calories of heat. As the decomposition is exothermic, the combination must be endothermic. Hence,

2g. hydrogen + *32g. oxygen* = *34g. hydrogen dioxid*—232 calories,
   (react with)   (to give)   (with an absorption of)

   and

34g. hydrogen dioxid = *2g. hydrogen* + *32g. oxygen* + 232 calories.
   (decomposes)   (and)   (with an evolution of)
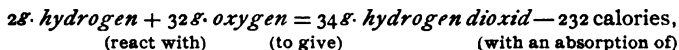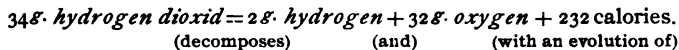
CONSERVATION OF ENERGY. The generalization of these facts leads to the law :

The amount of energy manifested in a reaction is equal to that manifested in the reverse reaction.

Thus, the energy given out as heat in the formation of a given mass of water is equal to that required in its decomposition. A mixture of 2 *g.* of hydrogen and 16 *g.* of oxygen contains 68,400 calories more heat than does 18 *g.* of water, and to get 2 *g.* of hydrogen and 18 *g.* of oxygen from water an amount of energy equivalent to 68,400 calories of heat must be put into the water. This is in accordance with the Law of the Conservation of Energy (§ 15).

OTHER FORMS OF ENERGY. Heat energy is not the only form that may be manifested in a chemical reaction ; other forms, as electrical, light, etc., are often observed. All these forms may, however, be converted into each other, and may be measured in the same units ; that of mechanical energy, the *erg*, is usually taken. A calory is equivalent to 4.2 million ergs and the electric unit of energy, the *joule*, to ten million ergs. The kind of energy to be employed in a reaction depends upon its nature. Thus, to decompose water into its elements, such a high temperature is required that it is ordinarily inconvenient to employ heat energy in that case. But electrical energy readily effects the decomposition of water, and we shall find it useful in many other reactions. The amount needed to decompose 18 *g.* of water is found, after the joules in which it is measured are converted into calories, to be 68,400 calories.

DECOMPOSITION AND DISSOCIATION. When hydrogen dioxid is heated it breaks up into water and oxygen, which, when the temperature is lowered, exhibit but a very slight tendency to re-form the dioxid; it is said to *decompose*. When water is heated, it vaporizes without decomposition, but if the steam be heated to a temperature of about 1,000°, a small fraction of it is found to break up into uncombined hydrogen and oxygen. With further rise of temperature this fraction increases until, when the temperature of about 2,800° is arrived at, half of the steam has been converted into free oxygen and hydrogen, and it is probable that at excessively high temperatures steam could not exist as such, but would be converted into its constituent gases.

Now it is found that on lowering the temperature the oxygen and hydrogen reunite to form steam. At every temperature between the extremely high one at which the elements only can exist and about 1,000°, there is a definite amount of steam broken up into oxygen and hydrogen; there is a state of equilibrium between the steam on the one hand and the elements, oxygen and hydrogen, on the other; just as much steam is produced in a given time as is decomposed in the same time. To a decomposition of this nature the name of *dissociation* has been assigned. Cases of dissociation are by no means uncommon, and several will be considered in some detail later.

Exercises

1. What physical constants of water are used in fixing certain units of measurement?

2. Why is it that insoluble substances, as sand, etc., have no characteristic taste?

3. How would you separate a mixture of sulfur, sand, and salt, so as to obtain all of each substance in a state of purity?

4. How would you determine the percentage of water in an apple?

5. Iron rusts in damp air. The rust is a compound of iron and oxygen. Where does the oxygen come from? What gas is formed during the rusting?

6. How may a mixture of hydrogen monoxid and of hydrogen dioxid be separated?

Problems

1. If water contains 11.19 per cent of hydrogen, how many grams of hydrogen are contained in 3.22 g. of water?

2. If 3.22 g. of water contain 0.36 g. of hydrogen, how many grams of the gas are contained in 100 g. of water?

3. If 6.44 g. of water contain 5.72 g. of oxygen, how many grams of oxygen are contained in 100 g. of water?

4. 10 $c.c.$ of hydrogen are mixed with 6 $c.c.$ of oxygen and the mixture exploded. How much water vapor is formed and how much gas is left? Which gas is it?

5. Van der Plaats in 1885 obtained 5.0834 l. of hydrogen by dissolving 20.6754 g. of zinc in dilute sulfuric acid. How many grams of water would be formed by the combustion of this amount of hydrogen, and what is the ratio of the weight of the zinc to the weight of the hydrogen?

6. 5 l. of hydrogen at 18° and 745 mm. are passed over heated copper oxid. What loss in weight does the oxid undergo? What is the weight of the water formed?

7. Dumas and Stas in 1843 performed Berzelius and Dulong's experiment, and found as the result of nineteen determinations that the loss in weight of the copper oxid was 840.161 g., and that 945.439 g. of water were formed. Find the ratio of combination of oxygen to hydrogen.

8. If 1 l. of steam at 150° and 721.0 mm. is condensed to water and the water totally decomposed by a current of electricity, how many grams of oxygen and of hydrogen will be obtained, and how many cubic centimeters will each of the gases occupy at 23° and 759 mm.?

9. Gypsum contains 17.65 per cent of water of crystallization. What volume of steam at 300° and 750 mm. is given off when all the water of crystallization of 100 g. of gypsum is expelled?

10. 32.3 $c.c.$ of hydrogen at 18° and 744 mm. are introduced into a eudiometer, and 56.8 $c.c.$ of oxygen at 20° and 745 mm. added. Which gas and how much of it at 21° and 745 mm. will be left after the explosion, if the tension of the aqueous vapor produced be taken into account?

11. Two volumes of hydrogen dioxid consist of two volumes each of oxygen and of hydrogen. If the dioxid could be vaporized without decomposition, what would be the weight of 1 l. of it, and what would be its specific gravity referred to hydrogen?

CHAPTER VI

NITROGEN AND ITS HYDROGEN
COMPOUNDS

HISTORICAL NOTE. Rutherford, in 1772, found that when an animal was placed in a confined portion of air, a certain gas incapable of supporting combustion remained even after the carbon dioxid given out by the animal had been removed. Scheele, however, was the first to recognize that this gas is a constituent of the atmosphere. Lavoisier gave the element the name *azote* (meaning *no life*), which it still bears in French; the name *nitrogen* was assigned it by Chaptal, because it occurs in niter.

68. Occurrence. Free nitrogen forms about four-fifths of the volume of the atmosphere. In combination it occurs in several minerals, as *niter* (saltpeter) and *Chile saltpeter*, and in many animal and vegetable substances.

69. Preparation. Nitrogen is ordinarily prepared by removing the oxygen from the air; the element is thereby obtained mixed with a small proportion (about one per cent) of other gases, principally argon. The substances commonly used to remove the oxygen are phosphorus and copper, because their oxids are solid and consequently easily separated from the nitrogen. Phosphorus set on fire in a confined portion of air combines with the oxygen, leaving the nitrogen and argon, and if the operation be conducted over water, the white smoke (phosphorus pentoxid) formed, being very soluble, is dissolved and thus separated from

the gases. (Fig. 15.) A solution of potassium pyrogallate will also absorb the oxygen from the air.

Nitrogen may be obtained from certain of its compounds free from argon. Thus, when ammonium nitrite or ammonium dichromate is heated, nitrogen is the sole gaseous product.

70. Properties. *Physical.* (Table I., Appendix *D.*) Nitrogen is a colorless, odorless, and tasteless gas, but slightly soluble in water.

Chemical. Nitrogen combines directly with but few elements. At high

Fig. 15 — APPARATUS FOR OBTAINING NITROGEN FROM THE AIR BY BURNING PHOSPHORUS

temperatures it unites with some metals, notably magnesium, forming compounds called *nitrids*. Electric sparks passed through mixtures of oxygen and nitrogen cause the elements to unite slowly (Fig. 9).

ARGON

HISTORICAL NOTE. Although nothing perhaps has received more attention chemically than has the air, yet it was not until 1894 that two English scientists, Rayleigh and Ramsay, found that what had always been taken for pure nitrogen really contained another elementary gas. This discovery has been aptly called the "triumph of the third decimal," for Rayleigh was led

to suspect the presence of the new gas in the air from the fact that the density of nitrogen from the atmosphere differed in the third decimal place from that of nitrogen prepared from chemical compounds.

PREPARATION. When a series of electric sparks is passed through a confined portion of air, the oxygen and nitrogen gradually unite to form compounds soluble in water, and hence easily removed. (Fig. 9.) By admitting enough oxygen to combine with the nitrogen, a gaseous residue remains, consisting mainly of argon. Cavendish performed this experiment towards the end of the eighteenth century, but did not examine the product carefully and had no suspicion as to what it really was. Argon may also be prepared by passing pure air, *i. e.*, air containing only oxygen and nitrogen (*argon*), over red-hot copper to remove the oxygen, and over red-hot magnesium to remove the nitrogen; the residue is argon.

PROPERTIES. Argon is a colorless, odorless, tasteless gas, somewhat more than twice as soluble as nitrogen in water. It forms no chemical compounds and may be said to have no chemical properties. For this reason its discoverers gave it the name of argon, derived from a Greek word meaning *inactive*.

AMMONIA

HISTORICAL NOTE. *Sal ammoniac*, a compound containing ammonia, has been known from very early times. Priestley, in 1774, first prepared and studied ammonia.

71. Occurrence. Ammonia is sometimes found in very small amounts in rain water, it having been formed during thunder storms by the action of lightning on the hydrogen of water and the nitrogen in the atmosphere. Several of its compounds occur in volcanic soils and in some animal secretions.

72. Preparation. Ammonia is commonly prepared in the laboratory by the action of slaked lime on some of its compounds or by heating its aqueous

solution ("ammonia water"). It was formerly manufactured by heating such animal substances as hair, horns, and hoofs with lime, and collecting the gaseous products. Coal used in the making of illuminating gas by the "old process" (page 91) gives a small amount of ammonia, which is separated from the other gases by passing their mixture through water in which the ammonia dissolves. This "wash water," when heated with slaked lime, gives off the ammonia it contains.

73. Properties. *Physical.* Ammonia is a colorless gas with a very pungent odor and a bitter taste. It is extremely soluble in water, with which it combines to form *ammonium hydroxid*. Several porous solids, especially charcoal, adsorb large proportions of the gas.

NOTE. To distinguish the absorption of a gas by a liquid from its "absorption" by a solid, the latter process is called *adsorption* and the former, *solution*.

Chemical. Ammonia dissociates at high temperatures; if it be passed through a porcelain tube containing iron or copper, and heated to redness, a mixture of one volume of nitrogen to three of hydrogen is obtained for each two volumes of ammonia used. While ammonia does not burn in the air, it does so when heated in pure oxygen; four volumes of ammonia and three of oxygen combine to form two volumes of nitrogen and six of water vapor. Ozone effects the immediate oxidation of ammonia.

LIQUID AMMONIA. Faraday, in 1823, placed a little of the solid compound which ammonia forms with silver chlorid in the rounded end of a stout bent tube

(Fig. 16). He then drew out the open end in a flame and sealed it off. As the solid compound dissociates into ammonia and silver chlorid when heated, the ammonia gas formed, being confined in a relatively small space, is subjected to pressure enough to liquefy it, especially if the temperature be reduced by putting the part of the tube not containing the silver compound in a freezing mixture.

Fig. 16—FARADAY'S AP-
PARATUS FOR PRODUC-
ING LIQUID AMMONIA

Liquid ammonia is much used as a refrigeratory agent and in the production of artificial ice (Fig. 17). Gaseous ammonia is forced by a compression engine into a series of pipes cooled by water flowing over them, and there liquefied by pressure. The liquid ammonia is then run into another series of pipes surrounded by brine and allowed to expand. The heat required to vaporize the ammonia again is abstracted from the brine, which is thus cooled down to a temperature of about $-20°$. This cold brine is made to circulate in a system of pipes, thus lowering the temperature of the rooms in which they pass; by encircling tanks of water with such a system of pipes the temperature of the water is lowered sufficiently to convert it into ice.

REVERSIBLE REACTIONS AND CHEMICAL EQUILIBRIUM. Ammonia under the action of electric sparks breaks up into nitrogen and hydrogen and these gases under the same influence form ammonia. Whether the reaction will proceed in one direction or the other depends upon the relative masses of the reacting substances, all other conditions remaining the same. Now it has been found that if a series of sparks be passed through a mixture of hydrogen and nitrogen in the proportions to form ammonia, after a time they will cease to combine. Also if sparks be passed through ammonia, after a while it will stop dissociating. The composition of the final mixtures in both cases is found to be the same, *viz.*, 2 per cent of ammonia gas and 98 per cent of the mixture of the gaseous elements. The two opposite reactions tend toward the same state of equilibrium. The fact that nitrogen and hydrogen under the influence
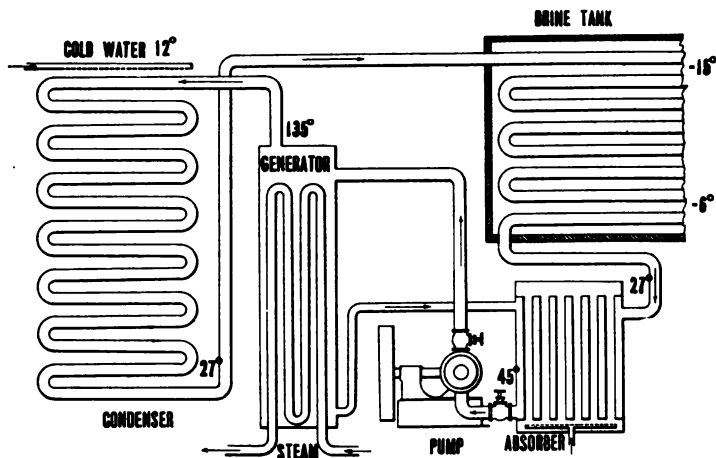
Fig. 17 — APPARATUS FOR PRODUCING LIQUID AMMONIA FOR REFRIGERATORY
PURPOSES

of electric sparks tend to produce ammonia may be
indicated thus :

Nitrogen + hydrogen → ammonia

and that ammonia dissociates into its constituent ele-
ments under the same influence,

Ammonia → nitrogen + hydrogen

the arrows pointing towards the product of the reac-
tion. The two expressions may be combined :

Nitrogen + hydrogen ⇄ ammonia
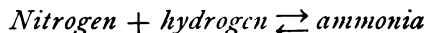
The sign ⇄ expresses very neatly the nature .of a
reversible reaction. It indicates that the reaction pro-
ceeds both ways, and also suggests the equality sign
which shows that the Law of Persistence of Mass is
followed. If the mixture of hydrogen and nitrogen
be in just the proportions to form ammonia and is
"sparked" in a eudiometer where water is the liquid,
the ammonia will be dissolved as soon as formed, and
thus removed from the field of action so that it is pos-
sible to make all of the mixture combine.

IMPORTANT NUMERICAL RELATIONSHIPS. A liter of ammonia at o° and 760 $^{mm.}$ of mercury weighs 0.765 $^{g.}$, of which 0.63 $^{g.}$ is nitrogen and 0.135 $^{g.}$ is hydrogen. It is to be noticed that these numbers are in the integral ratio of 17 : 14 : 3.

74. Uses. Ammonia is used in the manufacture of ice, and in aqueous solution for laundry purposes ("ammonia water"); also in the manufacture of washing soda, anilin dyes, and indigo.

HYDRAZIN AND HYDRAZOIC ACID

HISTORICAL NOTE. The elements hydrogen and nitrogen form besides ammonia three other compounds. These do not occur in nature, have been discovered only in the last few years, and are prepared by reactions too complicated to be discussed here.

Hydrazin is a colorless gas, one volume of which consists of two volumes of hydrogen to one of nitrogen. It resembles ammonia in a number of particulars.

Hydrazoic acid is also a colorless gas, but has properties the direct opposite of those of ammonia and hydrazin. It is very explosive and so are its compounds. Ammonia combines with it to form the fourth compound of nitrogen and hydrogen, two volumes of which contain three volumes of nitrogen and one of hydrogen.

Exercises

1. Why was the name "spirits of hartshorn" formerly applied to ammonia?

2. What is the difference between ammonium hydroxid and liquid ammonia? ·

3. Why does ozone effect the oxidation of ammonia at ordinary temperatures, while oxygen does not?

4. Given a jar containing equal volumes of ammonia, oxygen, and nitrogen, how can two of these gases be removed so as to leave the third in a state of purity?

5. How may it be shown experimentally that ammonia consists of nitrogen and hydrogen?

Problems

1. If a liter of ammonia under standard conditions weighs 0.765 *g·*, what is its specific gravity referred (*a*) to hydrogen, (*b*) to oxygen as a standard?

2. What is the ratio of the speeds of transpiration of ammonia and nitrogen?

3. What volumes of nitrogen and of hydrogen are required to make 600 *c. c.* of ammonia?

4. What volume of oxygen will just combine with the hydrogen obtained by passing electric sparks through 200 *c. c.* of ammonia until a state of equilibrium is arrived at?

5. When 100 *c. c.* of ammonia at 18° and 1,067 *mm.* are totally decomposed, how many cubic centimeters of nitrogen at 22° and 864 *mm.* are obtained?

6. 10 *g·* of ammonia were passed over red-hot copper. How much nitrogen and how much water was produced?

7. What volume of nitrogen at 25° and 724 *mm.* can be obtained from the decomposition of 876 *c. c.* of ammonia at 20° and 738 *mm.*?

8. 265 *c. c.* of ammonia at 21° and 742 *mm.* were burned in oxygen. How many cubic centimeters of nitrogen at 18° and 745 *mm.* were formed?

9. A solution contains 18 per cent, by weight, of ammonia. What volume of ammonia at 26° and 745 *mm.* will be obtained when 11 per cent of it is expelled from 500 *c. c.* of the solution?

10. What volume of oxygen under normal conditions is required to combine with the hydrogen contained in 600 *c. c.* of ammonia?

11. A sample of ammonium hydroxid contains 13 per cent of ammonia. How many liters of ammonia at 100° and 748 *mm.* can be obtained from 75 *g·* of the ammonium hydroxid solution?

12. Ammonium chlorid contains 31.8 per cent of ammonia. How many liters of ammonia at 0° and 760 *mm.* can be obtained from 50 *g·* of ammonium chlorid?

CHAPTER VII

CARBON

75. Occurrence. Carbon is very widely distributed in nature. The element in the crystallized state forms diamond and graphite. Associated with organic matter which has not been wholly destroyed, it forms fossil carbon or coal. Combined with certain other elements, principally hydrogen, oxygen, and nitrogen, it is the essential element of all organic matter, both vegetable and animal.

76. General Properties. All varieties of carbon have the following properties: They are solids which are infusible and involatile except at the highest temperatures; they are insoluble in all solvents except some molten metals, especially iron; they are combustible and yield eleven-thirds of their own weight of carbonic acid gas.

77. Diamonds. Diamonds owe their value as gems (1) to their scarcity, being found in only a few places on the earth, (2) to their hardness, and (3) to their great brilliancy, due to their high refractive index or power of bending rays of light. Black diamonds, called *carbonado*, are also found, which, while not used as gems, are employed in the manufacture of drills for rocks. The conditions required for the formation of diamonds in nature seem to be the crystallization of molten carbon under enormous pressure. These conditions have been realized approximately in the laboratory, and

very small artificial diamonds have been prepared in the following manner: Iron was melted at the high temperature of the electric furnace (page 115) and carbon dissolved in it. When the mixture was suddenly cooled by immersing it in cold water, a crust of solid iron formed, which, contracting as it cooled, exerted the necessary pressure. The iron was then dissolved in an acid, leaving a residue of diamonds. Diamonds may be burned by heating them in an atmosphere of oxygen. When heated away from oxygen to about 1,500°, they become changed into a product resembling graphite.

78. Graphite. Graphite is quite abundantly diffused over the earth. It is also manufactured in an electric furnace. If any variety of carbon is dissolved in molten iron, graphite is formed when the iron cools slowly, and may be obtained by dissolving away the iron in nitric acid.

Graphite has a grayish-black color and a metallic luster; hence the names, *black lead* and *plumbago* (the Latin word for lead is *plumbum*). It seems soft, leaves a black mark when rubbed over paper, and has a greasy feel, so that it is adapted for use as a lubricant. It is a fairly good conductor of heat and electricity. It is used in the manufacture of motor and dynamo brushes, electrodes, conducting surfaces in electrotyping, paint, stove polish, and "lead" pencils. For this last purpose the graphite is powdered, mixed with clay, and the plastic mass forced through an iron cylinder having small holes in one end, from which it issues in the form of wires. These are cut into suitable lengths and fixed in grooved sticks.

Graphite resists the action of heat so well that it is used in making crucibles and stove polish. It can be burned only at extremely high temperatures in an atmosphere of oxygen, or when heated with some oxidizing agent, as potassium chlorate.

COAL

79. Occurrence. Coal is found in a great many places; hardly a country is entirely without it. Something like 300,000,000 tons are mined annually, and it is estimated that the supply is sufficient to cover the earth with a layer three feet thick.

80. Formation. Coal was originally vegetation, and is the charred remains of vast forests which covered large portions of the earth's surface in remote geological ages. Slow subsidence of the earth's crust caused these forests to be covered with mud and sand. The buried wood decayed slowly, whereby the volatile compounds formed by the decomposition of the wood escaped, leaving the involatile portions. Subsequent changes in the earth's strata brought it about that these coal beds were buried deeper and deeper, and in some cases tilted from their original horizontal position. The weight of the strata above the coal exerted enormous pressure, so that it was compressed into massive blocks. The longer this process lasted, the purer the carbon. Graphite seems to be the product of the completed process.

Hard coal or anthracite may contain as much as 90 per cent of carbon, and bituminous coal up to 70 per cent, although the percentages are oftener less. Even at the present time vegetation, especially some

mosses, is commencing to turn into coal. Peat, containing about 40 per cent of carbon, is in the first stages. Peat, soft coal, and anthracite are the main successive steps in the decomposition of vegetation.

Anthracite is hard, brittle, and shiny, burns with almost no flame, and requires a high temperature to ignite it. It is much used in heating houses, etc., but is more expensive and less abundant than bituminous coal.

Bituminous coal is softer and less shiny than anthracite and ignites at a lower temperature. It burns with a good deal of flame, and some of its carbon usually escapes as smoke.

Lignite or *brown coal* has been formed more recently than soft coal; it often preserves the structure of the original wood and burns with a long flame, producing much smoke.

Jet is a very hard and black variety of lignite which takes a fine polish, and is used in making certain articles of jewelry.

81. Charcoal. The primitive method of preparing charcoal is by piling wood in a conical heap and covering it with earth and sod; small openings are left so that just enough air may be admitted to burn a portion of the wood, and thus generate heat enough to char the rest. The gases formed are water vapor, compounds of carbon and hydrogen, carbonic acid, etc., while some acetic acid, wood spirit, and tarry matter are also produced. The finer grades of charcoal, such as are used in the manufacture of gunpowder, are prepared by heating wood in iron retorts. Charcoal contains a little mineral matter which was present in the wood.

82. Boneblack or Bone Char. Boneblack or bone char is obtained by the destructive distillation

of bones. It is mixed with a considerable proportion of the mineral constituents of bones. A finer grade is made by charring blood.

83. Properties and Uses of Charcoal and Boneblack. Charcoal is a brittle and porous solid with neither taste nor odor. It is a pretty good conductor of electricity, but a poor conductor of heat. It is insoluble in all liquids except molten iron, and can be melted and vaporized only at extremely high temperatures. It resists the action of air and moisture very well. Wooden posts may be made more durable by charring the surface in contact with the ground. Charred piles have been found in a state of good preservation even after the lapse of over 2,000 years.

Boneblack is usually met with in the form of black grains.

The chief use of charcoal is as a fuel. It burns with almost no flame. It is valuable as a reducing agent, and is therefore extensively used in separating metals from their ores when these are oxids.

Charcoal has the remarkable property of adsorbing gases and condensing them in its pores. This property is utilized in the sweetening of foul water and tainted meat. To this property is to be ascribed the deodorizing and disinfecting action of charcoal, which seems to be due to the oxygen condensed in the pores of the charcoal. This condensed oxygen is especially active in combining with the gases given off by putrefying matter. Thus, a dead animal packed in charcoal emits no odor, but its decomposition is hastened. Charcoal also has the power of removing coloring matters from solution, but

boneblack is much superior in this respect, and is extensively used in sugar refineries to clarify syrups.

84. Lampblack. Lampblack is prepared by burning pitch or tarry combustibles in a limited supply of oxygen (air) so that much soot is formed. This soot is conducted into chambers hung with sacking, where it is deposited. Lampblack is used in the manufacture of printers' ink, paint, and shoe-blacking.

85. Coke. When soft coal is subjected to destructive distillation it decomposes into volatile products, from which illuminating gas and coal tar are obtained, and into an involatile, porous, grayish residue known as *coke*. Coke ignites only at high temperatures, burns without smoke and with but little flame, giving a very hot fire. It is used as a reducing agent in the extraction of metals and to a limited degree for heating purposes.

86. Gas Carbon. Some of the gaseous compounds formed in the manufacture of coke are decomposed on coming in contact with the hotter parts of the retort, and the carbon in them is deposited. This gas carbon resembles graphite, and as it is a good conductor of electricity, is used in electric batteries and in arc lights.

Exercises

1. What property of carbon in any of its forms constitutes its best test?

2. Can stove-blacking be used as shoe-blacking? Can shoe-blacking be used as stove-blacking?

3. How may any form of carbon be converted in part into graphite?

4. The filaments of incandescent lamps consist of carbon. What does the fact that the interior of the bulbs gradually

becomes covered with a dark coating indicate (a) as to the temperature of the glowing filament, (b) as to the volatility of carbon?

5. Which forms of carbon occur in nature? Which are crystalline?

6. How may the chemical identity of the various forms of the element carbon be proved?

7. Why is charcoal used in the lining of certain makes of refrigerators?

8. What are the advantages and disadvantages of the following fuels: (1) hard coal, (2) soft coal, (3) coke, (4) charcoal?

9. Which of the elements thus far studied occur in different allotropic modifications? Which of these allotropes are the most stable?

10. What reducing agents have been found among the various forms of the elements studied?

THE COMPOUNDS OF CARBON WITH OXYGEN

87. Combining of Carbon and Oxygen. Whenever any form of carbon is heated to a sufficiently high temperature in air or oxygen, combination takes place, accompanied with heat and light. If the oxygen be present in considerable excess and if the gaseous products be removed from the carbon as fast as formed, only one compound of the two elements is produced; this is variously known as *carbon dioxid, carbonic acid gas*, or *carbonic anhydrid*. If, however, the oxygen be limited in amount, and especially if the products remain in contact with the burning carbon, another compound named *carbon monoxid* is also formed. Both these compounds are gases, and they are the only compounds of carbon and oxygen known.

CARBON DIOXID

88. Occurrence. Carbon dioxid normally occurs free in the atmosphere to the extent of about 0.04 per cent. The percentage is higher in cities, especially near factories employing steam power, than in the country or above the sea. The oxids of many metals combine with carbon dioxid to form *carbonates*, some of which form immense deposits, as limestone and marble (calcium carbonate), and magnesite (magnesium carbonate). Chalk, coral, and the

shells of crustaceans and molluscs are mainly composed of calcium carbonate.

89. Formation and Preparation. Whenever carbon in any of its modifications or any compound of carbon is burned with a liberal supply of oxygen, carbon dioxid is formed. It is also produced in fermentation and in most kinds of decay. Formed in the tissues of animals, it is carried to the lungs by the blood and is exhaled in respiration. Chemical processes in the earth's interior often produce it, and the waters of some springs are charged with it. It is the miner's "choke damp," formed by the combustion of "fire damp" (§ 102).

The most convenient way of preparing carbon dioxid in a state of purity is by the action of an acid upon a carbonate. With but few exceptions all acids will liberate this gas from a carbonate.

The industrial methods of obtaining carbon dioxid are, (1) the action of dilute sulfuric acid on bicarbonate of soda, (2) the heating of limestone, (3) the collecting of the gas that is given off from the fermenting liquid from which beer is made.

90. Properties. *Physical.* Carbon dioxid is a colorless, odorless gas with a rather sharp taste. It is much heavier than air, and sometimes collects in hollows of the ground or in wells and cellars, when it is produced more rapidly than it can diffuse away into the atmosphere. There is a cave in Italy called the "Dog's Cave" (*Grotto del Cane*) which is partially filled with carbon dioxid. A man may enter the cave with impunity, but a dog is promptly suffocated. The reason is, that the layer of the heavy gas does not reach up to a man's nostrils, but a dog

is completely immersed in it. It is wise before entering an old well or cellar to take the precaution of lowering into it a lighted candle or lantern; if it goes out, carbon dioxid is probably present. The gas may be removed by introducing powdered quicklime or ammonia, which absorb it.

At ordinary temperatures carbon dioxid may be converted into a liquid by a pressure of about fifty atmospheres. If this pressure be removed, the limpid, colorless liquid changes into a gas so rapidly that, as heat is required for the vaporization of a liquid, a portion is converted into a white solid, resembling snow. This wastes away but slowly and may be handled. It does not seem cold to the hand, because a layer of poorly conducting gas separates it from the skin. But if it be pressed between the fingers, it has the same effect as a red-hot iron.

Carbon dioxid gas is somewhat soluble in water; at ordinary temperatures a volume of the gas dissolves in about an equal volume of water. With increase of pressure there is an increase of solubility of the gas.

Chemical. At temperatures above 1,300° carbon dioxid dissociates into oxygen and carbon monoxid; electric sparks also produce the same effect. A magnesium wire or ribbon ignited in the air and then plunged into a jar of carbon dioxid continues to burn; carbon is deposited on the sides of the jar. Carbon dioxid combines with ammonia, lime, and all of the class of substances known as hydroxids to form carbonates. In sunlight, chlorophyll, the green coloring matter of plants, decomposes carbon dioxid and sets oxygen free.

91. Uses. The sparkling appearance and sharp taste of most mineral waters are due to the carbon dioxid they hold in solution. "Soda water" is water charged with the gas. In beer and champagne carbon dioxid is generated by fermentation, dissolves in the liquid, and, when the cork of the bottle is removed, escapes and produces the foaming and liveliness of the liquor.

CARBON MONOXID

92. Preparation. Formic acid when heated with strong sulfuric acid decomposes into carbon monoxid and water. It is more convenient to use sodium formiate; the products are then the monoxid and sodium sulfate. Oxalic acid when heated decomposes into carbon monoxid, carbon dioxid, and water. As oxalic acid volatilizes somewhat at the temperature where the decomposition sets in, it is generally heated with strong sulfuric acid; the decomposition then proceeds at a lower temperature. The carbon dioxid is removed by passing the mixture of gases through a solution of potassium hydroxid. The monoxid may also be obtained by heating potassium ferrocyanid with sulfuric acid.

The industrial method consists in passing the gaseous products of the combustion of coal over red-hot coke. The carbon dioxid is thus reduced to carbon monoxid.

93. Properties. *Physical.* Carbon monoxid is a colorless and tasteless gas. When pure its odor is scarcely perceptible; it is very slightly soluble in water.

PROUST

BERTHOLLET

DALTON

DAVY

FARADAY

Plate III

CLAUDE LOUIS BERTHOLLET

1748-1822; French

Close friend and adviser of Napoleon I. First to consider the influence of relative masses on the nature of a reaction

JOSEPH LOUIS PROUST

1778-1850; French

Established Law of Definite Proportions by Weight. Made many analyses that were accurate for his time

JOHN DALTON

1766-1844; English

Modified the ancient hypothesis of atoms to account for Laws of Definite and Multiple Proportions, the second of which he discovered

MICHAEL FARADAY

1791-1869; English

Liquefied ammonia, chlorin, and other gases. Discovered relationship between equivalents of elements and quantities of electricity

HUMPHREY DAVY

1778-1829; English

Applied electrolytic methods and isolated thereby sodium, potassium, calcium, barium, and strontium. Inventor of miners' lamp bearing his name

Plate III

Chemical. Carbon monoxid burns with a pale blue flame, forming carbon dioxid. At high temperatures it reduces many metallic oxids.

Physiological. On account of its action on the blood, carbon monoxid is very poisonous. Hæmoglobin, the red coloring matter of the blood, combines when in the lungs with the oxygen of the air. If, however, carbon monoxid be present in the air breathed, it forms with the hæmoglobin a more stable compound than does oxygen, so that the blood cannot exercise its vital functions.

94. Uses. Carbon monoxid is employed as a reducing agent in the manufacture of iron and steel.

Combustion in a Coal Stove. When the draft is open, air enters in abundance at *A* (Fig. 18) and, combining with the lower layers of coal which are very hot, forms carbon dioxid. As this passes up through the hot coal it is robbed of nearly half of its oxygen, which combines with more coal, so that carbon monoxid is produced. When this gas reaches the top of the coal where plenty of air is entering at *D*, however, it combines with the oxygen of the air, burning with a pale blue flame, and producing carbon dioxid again. If the back draft at *E* be closed, but little air enters at the stove door; consequently some of the carbon monoxid may not be burned and may escape into the room through *D*.
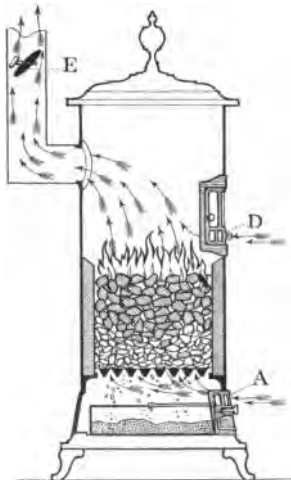
Fig. 18 — COMBUSTION IN A COAL STOVE

Composition of the Oxids of Carbon; Carbon Dioxid. Lavoisier put some fragments of diamond in a crucible supported above a vessel

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containing mercury and placed a jar full of oxygen over it. On concentrating the sun's rays on the diamond by means of a large lens, he found it to gradually disappear. After the apparatus had cooled to the original temperature he observed that the volume of the gas was the same as at first.

Carbon dioxid contains an equal volume of oxygen.

CARBON MONOXID. Berthollet introduced into an eudiometer ten volumes of carbon monoxid and ten volumes of oxygen. After passing the spark he found the residue to be composed of five volumes of oxygen and ten volumes of carbon dioxid. Hence, carbon monoxid unites with half its volume of oxygen to form a volume of carbon dioxid equal to the volume of carbon monoxid taken. But carbon dioxid contains its own volume of oxygen ; consequently :

Carbon monoxid contains only half as much oxygen as does the same volume of the dioxid.

Dumas and Stas found that when the various forms of pure carbon were burned to form carbon dioxid, the ratio of the weight of the carbon to that of the oxygen was 12 : 32, and Stas determined the ratio of the mass of carbon to that of oxygen in carbon monoxid to be 12 : 16. Carbon dioxid is thus seen to contain twice the mass of oxygen that the monoxid does.

The above results are excellent illustrations both of the Laws of Definite Proportions by Mass and by Volume, and of the Law of Multiple Proportions.

SOME NUMERICAL DATA. One liter of carbon monoxid weighs 1.251 ^{g}, of which 0.715 ^{g} is oxygen and 0.536 ^{g} carbon. The weight of carbon and oxygen in one liter of carbon dioxid weighing 1.966 ^{g} is 0.536 ^{g} and 1.43 ^{g}, respectively.

ENERGY RELATIONSHIPS OF CARBON AND ITS OXIDS. When 12 ^{g} of charcoal, graphite, or diamond are burnt so as to produce 44 ^{g} of carbon dioxid, the number of calories evolved is 97,650, 94,810, and 94,325, respectively. The diamond is thus seen to contain less energy than graphite, and graphite less than charcoal. The allotropic modifications of other elements also contain different amounts of heat energy. Allotropic forms

differ then not only in their material properties, but also in the amounts of energy they contain.

It is impossible to burn any form of carbon so as to produce the monoxid without some admixture of the dioxid. The heat of combustion of carbon monoxid cannot therefore be determined directly. 28 $g.$ of carbon monoxid, however, unite with 16 $g.$ of oxygen to produce 44 $g.$ of carbon dioxid with an evolution of 68,170 calories. Now, as in the combustion of 12 $g.$ of charcoal to 44 $g.$ of carbon dioxid 97,650 calories are given out, we find by subtraction that the heat effect of the union of charcoal and oxygen to form carbon monoxid is equal to 97,650 − 68,170 = 29,480 calories.

This procedure illustrates what has often to be done in measuring the changes of heat energy in reactions. Comparatively few reactions are of such a nature that the heat evolved or absorbed can be directly measured. Usually several intermediate reactions whose heat effect is such as can be directly determined have to be employed. The investigation of such cases has led to the discovery of the Law of Constant Heat Summation, first formulated by the Russian, Hess, in 1840 :

The amount of heat given out or taken in by a system of substances undergoing chemical change depends only upon the initial and final states of the system.

Thus, carbon may unite with oxygen to form the dioxid in one of two ways : (1) It may be burned in such a way that no carbon monoxid is produced, or (2) its combustion may be attended with the formation of more or less of the monoxid which afterward unites with oxygen to give the dioxid. The initial state of the system is a mixture of carbon and oxygen the final state is the compound, carbon dioxid ; an intermediate state may be a mixture of both oxids. Now, the law affirms that no matter what the intermediate states of the system, the heat liberated depends only upon the initial and final states.

In many cases a considerable number of intermediate reactions have to be considered before a certain compound can be made to yield the desired one. The heat effect of each has to be determined. Simple algebraical operations then give the desired datum.

Exercises

1. Carbon dioxid is heavier than air. Why then does it not occur in greater and greater proportion near the earth's surface?

2. How can the oxids of carbon be changed the one into the other? What general processes do the changes illustrate?

3. Show how the oxids of carbon are an illustration of the Laws of Definite Proportions and of Multiple Proportions both by volume and by weight.

4. What tests would you propose for carbon monoxid and for carbon dioxid?

5. How would you separate a mixture of the oxids of carbon?

6. Suppose you have a jar containing a mixture of equal volumes of carbon dioxid, oxygen, and of nitrogen. How can you remove two of the gases so as to leave the third?

7. How can it be proved experimentally that oxalic acid and also formic acid contain carbon?

Problems

1. What per cent by weight of carbon is contained in (*a*) carbon monoxid; (*b*) carbon dioxid?

2. How many times faster does oxygen diffuse than carbon dioxid?

3. How much water has to be decomposed to yield enough oxygen to form with carbon 44 *g.* of carbon dioxid?

4. The annual consumption of coal in a certain chemical plant amounts to 190,000 tons. Counting 310 working days to the year, how many tons of carbon dioxid are daily thrown out into the atmosphere, if on an average the coal contains 70 per cent of carbon?

5. Roscoe in 1882 obtained on burning 6.4406 *g.* of diamonds, 23.6114 *g.* of carbon dioxid. How much carbon dioxid could be obtained from the burning of 12 *g.* of diamonds?

6. What weight of oxygen is required to burn a diamond weighing 0.43 *g.* and containing 0.03 per cent of an incombustible impurity?

7. A diamond weighing 3.2678 *g.* is burned in oxygen, leaving an ash amounting to 0.0007 *g.* What is the volume at 0° and 760 *mm.* of the carbon dioxid formed?

8. 25 *l.* of carbon monoxid at 22° and 745 *mm.* are required. What volume of carbon dioxid at 18° and 740 *mm.* must be passed over red-hot carbon to yield this amount of the monoxid?

CHAPTER IX

SOME NITROGEN AND HYDROGEN COM-
POUNDS OF CARBON

CYANOGEN

95. Occurrence. Carbon forms but one compound with nitrogen. This is called cyanogen (blue generator), because it occurs in some blue-colored compounds.

96. Preparation. Refuse animal matter which contains carbon and nitrogen, such as blood and horn, is heated with iron and potash. The product is potassium ferrocyanid (yellow prussiate of potash). When this is fused with potassium carbonate, potassium cyanid is produced, which in turn reacts with mercury compounds to give mercuric cyanid, and this when heated decomposes into mercury and cyanogen.

97. Properties. Cyanogen is a colorless gas which is easily condensed into a liquid. It burns with a purplish flame; one volume of the gas combines with two volumes of oxygen to yield two volumes of carbon dioxid and one volume of nitrogen. It is extremely poisonous.

HYDROCYANIC ACID

98. Occurrence and Preparation. Hydrocyanic acid occurs in nature in combination with other substances, also in bitter almonds and cherry leaves.

It is prepared by the action of dilute sulfuric acid on potassium cyanid.

99. Properties. Hydrocyanic acid is a colorless, volatile liquid with an odor something like that of peach kernels. It mixes with water in all proportions, and its aqueous solution is known as *prussic acid*. It is one of the most deadly of all known poisons.

COMPOUNDS OF CARBON AND HYDROGEN; HYDROCARBONS

100. Organic and Inorganic Chemistry. Animal and vegetable substances, with hardly an exception, contain carbon, and it was formerly believed that, except in a few cases, carbon compounds could be formed only through the agency of life or "vital force." The compounds of carbon being very numerous and important, they were formerly treated of in a special division of chemistry, called *Organic Chemistry*. But since 1827, more and more carbon compounds have been prepared artificially in the laboratory, and the distinction between organic and inorganic chemistry has been done away with. Still it has been found advisable to treat the compounds of carbon separately, because of their multiplicity and peculiar relationships. The name, "Organic Chemistry," is therefore retained, not to denote that it is the chemistry of the compounds obtained from the vegetable and animal kingdoms, but merely to indicate that it is the chemistry of the carbon compounds. Some few of these compounds, however, may profitably be studied in elementary inorganic chemistry.

101. Hydrocarbons. Hydrocarbons are compounds of hydrogen and carbon. They are very numerous and include such gases as acetylene and methane, such liquids as kerosene and turpentine, and the solids, vaseline, paraffin, and so on.

METHANE OR MARSH GAS

102. Occurrence. Marsh gas is one of the products of the decay of vegetable matter under water. By stirring up the mud in marshy places it may be made to rise to the surface in bubbles which also contain carbon dioxid and nitrogen. Methane frequently occurs in coal mines, probably formed by a decomposition of the coal, and is there called "fire damp."

103. Preparation. Methane is obtained in the laboratory by heating a mixture of sodium acetate, sodium or potassium hydroxid, and quicklime; a little hydrogen and ethylene is also formed.

104. Properties. *Physical.* Methane is a colorless, tasteless, odorless gas, but slightly soluble in water.

Chemical. Methane burns with a feebly luminous flame, yielding water and carbon dioxid; one volume of methane yields one volume of water vapor and one of carbon dioxid. Mixtures of methane and oxygen (or air), when in the proportions of one volume of methane to two or three volumes of oxygen (about eight volumes of air), explode violently when ignited. This explosive mixture is the cause of the terrible accidents which sometimes occur in coal mines. As carbon dioxid or "choke damp" is formed by the combustion of "fire damp," the

miners who may survive the explosion usually succumb from suffocation due to the former gas.

COMPOSITION. If sparks be made to strike through methane contained in an eudiometer, it is noticed that black particles appear, and that the volume of the gas increases until it is finally twice the original volume. An examination shows that the particles consist of amorphous carbon and that the gas is hydrogen. Methane therefore contains twice its volume of hydrogen. As carbon cannot be vaporized readily, its vapor density cannot be found, and its volume cannot be compared with that of the methane or the hydrogen. It may be weighed, however, so that the mass relationships can be ascertained. 1^l of methane weighs 0.716^g and the carbon obtained from it, 0.536^g. As 1^l of hydrogen weighs 0.09 ^{g}, we have the equation :

1^l of *methane* = 2^l of *hydrogen* + *carbon*
weighing 0.716^g (gives) weighing 0.180^g (and) weighing 0.536^g.

HEAT OF FORMATION OF METHANE. As hydrogen and carbon do not unite directly to form methane, its heat of formation cannot be determined by direct methods. It can, however, be ascertained by an application of the Law of Constant Heat Summation (page 83). 16^g of methane combine with 64^g of oxygen to produce 44^g of carbon dioxid and 36^g of water with an evolution of 211,900 calories of heat. We saw that 12^g of carbon (diamond) combine with 32 ^{g} of oxygen to form 44 ^{g} of carbon dioxid with an evolution of 94,320 calories, and 4^g of hydrogen unite with 32 ^{g} of oxygen to give 36^g of water with a liberation of 136,800 calories. In the formation of 44^g of carbon dioxid and 36 ^{g} of water, there are required 94,320+136,800=231,120 calories. As in the combustion of 16 ^{g} of methane to these quantities of water and carbon dioxid, 211,900 calories were liberated, the difference between the sums of the heats of combustion of carbon and of hydrogen, and the heat of combustion of methane, must give the heat of formation of methane. Calling this x, we have :

$$x + 211,900 = 94,320 + 136,800$$

or
$$x = 231,120 - 211,900 = 19,220$$

The heat of formation of methane is therefore 19,220 calories.

ETHYLENE OR OLEFIANT GAS

HISTORICAL NOTE. The properties of ethylene, discovered by Becher in the seventeenth century, were studied by four Dutch chemists toward the end of the eighteenth century. They gave it the name of olefiant (oil-making) gas because it combines directly with chlorin gas to form an oily liquid, ethylene chlorid or "Dutch liquor."

105. Preparation. Ethylene may be prepared by heating alcohol with strong sulfuric or with phosphoric acid. It is also formed with other products when such substances as wood or bituminous coal are subjected to destructive distillation.

106. Properties. *Physical.* Ethylene is a colorless gas with a slight odor, soluble in about a sixth its volume of water.

Chemical. At a red heat ethylene decomposes into acetylene and hydrogen. It burns with a brilliant flame. One volume of ethylene yields two volumes of water vapor and two of carbon dioxid. It is the chief light-giving constituent of illuminating gas obtained from the destructive distillation of coal.

ACETYLENE

107. Preparation. Whenever either ethylene or the vapor of alcohol is heated to redness, some acetylene is formed. It may be prepared from the elements by causing an electric arc to play between two carbon electrodes placed in an atmosphere of

hydrogen; this mode of preparation is historically very interesting, as being one of the first direct syntheses of an organic compound from the elements. The most convenient way to prepare it is by the action of water on calcium carbid.

108. Properties. *Physical.* Acetylene is a colorless, tasteless gas of a faint and rather pleasant odor when pure, and is soluble in about an equal volume of water.

Chemical. When heated nearly to a red heat, acetylene changes into benzene; six volumes give two volumes of benzene vapor. This peculiar reaction, *i. e.*, this property it has of combining with itself, is very characteristic. Many other organic compounds also can, under certain conditions, undergo such reactions, and the general phenomenon is known as *polymerization.* Acetylene burns with a brilliant flame; the products are carbon dioxid and water.

ACETYLENE AS AN ILLUMINANT. As calcium carbid can be made quite cheaply, and as it reacts with water to give acetylene, this gas, which burns under proper conditions with a very bright and agreeable light, has been introduced into use for the illumination of dwellings. Many forms of generators have been devised to that end. The safest form drops the carbid in small portions into the water, whereby the temperature is not raised as high as it is when the water is added to the carbid. At first it was proposed to compress the gas into steel cylinders and to connect these with the gas-piping of a house, but it was soon found that compressed acetylene was highly explosive, so that such a mode of using it had to be abandoned. Its explosiveness is due to its being an endothermic compound; once its decomposition is started, it proceeds with explosive violence because of the energy liberated.

109. Methane, Ethylene, and Acetylene Compared. The ratio of the weight of hydrogen to that of carbon in methane is 1 : 3; in ethylene, 1 : 6; and in acetylene, 1 : 12. The relative amounts of carbon are thus seen to stand in a very simple relationship. The ratios of the volumes of hydrogen entering into the composition of the gases are also very simple. Thus, two volumes of methane contain four volumes of hydrogen; two volumes of ethylene, two of hydrogen; and two volumes of acetylene, one of hydrogen. The less the proportion of hydrogen, the more brilliant and smokier the flame of the hydrocarbons. The only products of their total combustion are carbon dioxid and water.

ILLUMINATING GAS

HISTORICAL NOTE. It was known from early times that most vegetable materials, as wood, etc., when heated apart from the air, yielded gaseous products burning with a more or less brilliant flame, but it was not until the beginning of the nineteenth century that these gases were manufactured and distributed by systems of pipes for purposes of illumination.

MANUFACTURE BY THE OLD PROCESS. The manufacture of illuminating gas comprises five more or less distinct processes — the distillation of the vegetable material; the condensation of the liquid products carried along by the gas; the washing of the gas; the purification of the gas; the storing of the gas.

Distillation. Although wood or petroleum is sometimes used, yet bituminous coal is by far the commonest material employed. The coal is placed in ⌒-shaped retorts about six feet in length made of fire clay. The retorts are arranged in a furnace as shown in Fig. 19, and closed with iron plates provided with outlets; they are then heated to about 1,200°. The gaseous and volatile products of the distillation pass off, leaving the solid products, coke and gas carbon, behind.

HYDRAULIC MAIN

RETORT

FURNACE

CONDENSER

SCRUBBER

PURIFIER

GAS HOLDER
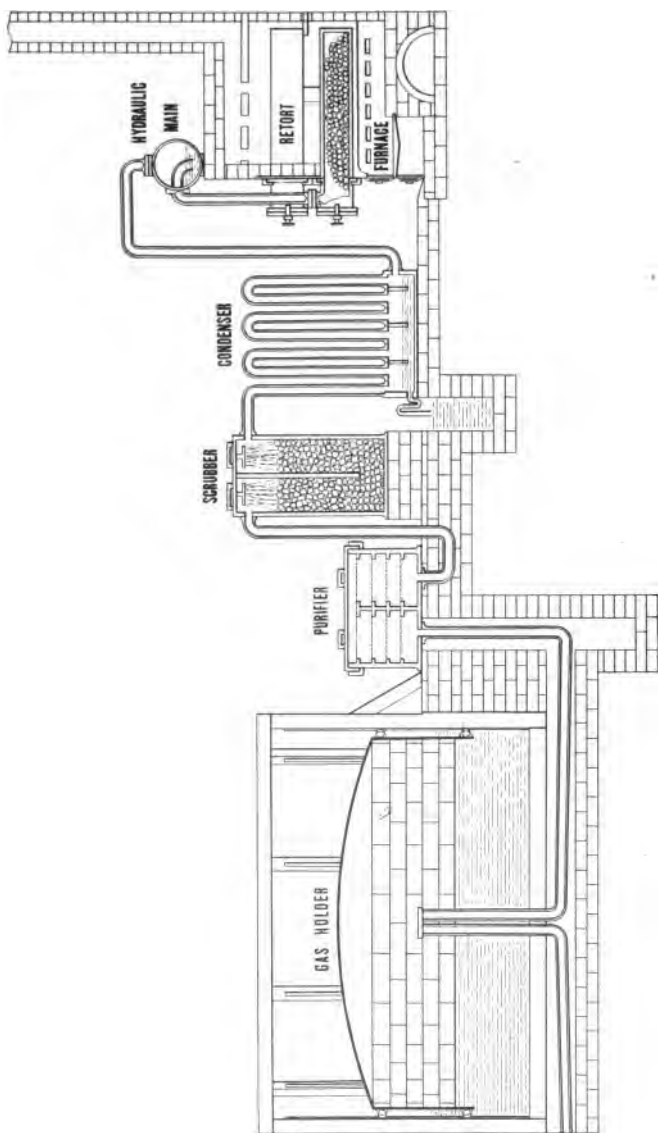
FIG. 19 — THE MANUFACTURE OF ILLUMINATING GAS FROM COAL BY THE OLD PROCESS

The volatile products pass up the "ascension" pipes, then down through the "dip" pipes and bubble through the water contained in the "hydraulic mains," where the less volatile products, such as tar and water, are in part condensed. The "coal tar" which is thus formed is distilled and many valuable products obtained from it.

Condensation. From the hydraulic main the gas passes into the "condensers," a series of vertical pipes set in an iron box filled with water. The temperature of the gas is now much lowered and most of the tar, oils, and ammonia carried along with it are deposited.

Washing. To remove the rest of the ammonia and some of the carbon dioxid and sulfur compounds, the gas enters the base of a tower called a "scrubber." This is filled with coke, brushwood, or wooden slats, and a spray of water made to trickle down it. The gas is thus broken up into little bubbles and is thoroughly exposed to the action of the water.

Purification. The impurities which still remain to be removed are traces of carbon dioxid and hydrogen sulfid, and the purifying material is slaked lime or some other material which absorbs the gases. The purifying substance is mixed with sawdust to make it spongy and porous, and spread out over trays with perforated bottoms. After circulating through the "purifier," the gas passes into the holders.

Storage. The gas holders are large, bottomless chambers floating upon a tank of water, and secured by a framework so as to move only up and down.

"WATER-GAS." The manufacture of illuminating gas by the method just described has been quite generally supplanted by the "water-gas" process. When steam is passed over white-hot coal, the former is partially dissociated (page 60). The oxygen then combines with the carbon, producing carbon monoxid, and a mixture of this gas with hydrogen is the main product. This "water-gas" burns with an almost colorless flame. It is used as a fuel, but has to be "enriched" with hydrocarbons in order to make its flame luminous. The process of manufacture is as follows :

The "generator" (Fig. 20) is charged with coal which is heated as hot as possible by means of a blast of

GENERATOR CARBURETER SUPERHEATER OIL HEATER WASHER SCRUBBER CONDENSER BLOWER
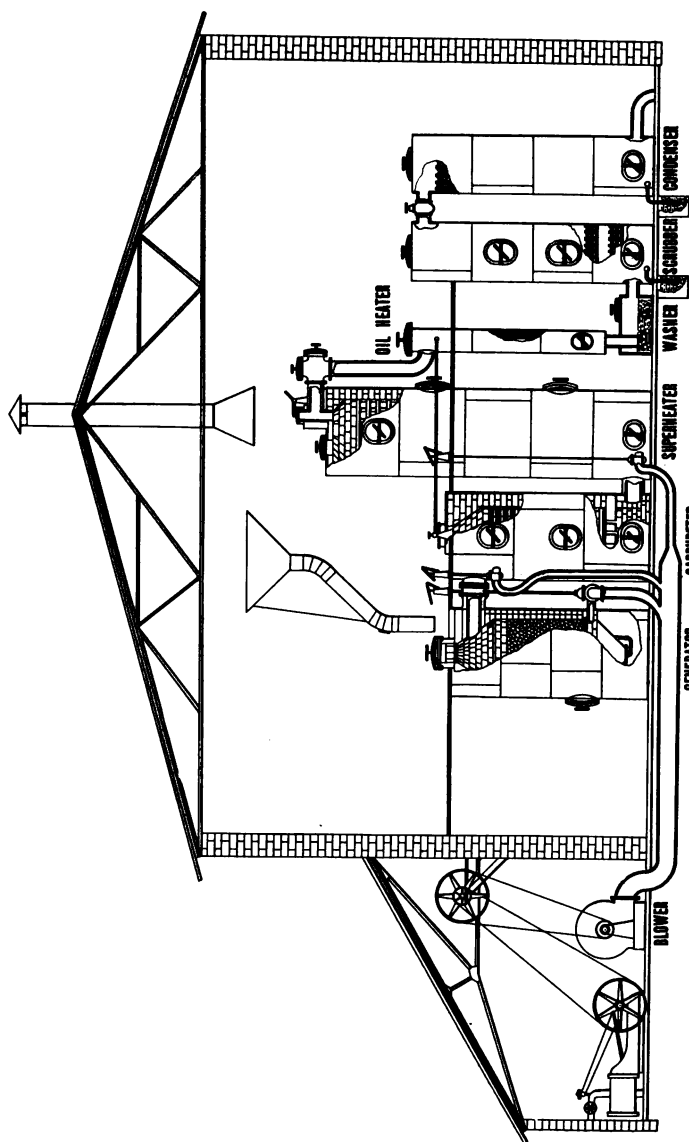
Fig. 20 — THE MANUFACTURE OF "WATER GAS"

air forced through it. This is then cut off and steam, also heated to a high temperature, blown through the coal, whereby the reaction stated above takes place. The mixture of hydrogen and carbon monoxid is then led to the "superheaters" in which low boiling hydrocarbons are being decomposed so as to furnish the gaseous hydrocarbons which impart illuminating power to the gas. The resulting mixture of gases is then forced through the "washer," "scrubber," and "condenser" (these are essentially the same as used in the "old process") to remove any undecomposed liquid hydrocarbons or any carbon dioxid.

PROPERTIES OF ILLUMINATING GASES. Illuminating gases are colorless, have a disagreeable odor, and are but very slightly soluble in water. Water gas is more poisonous than old-process gas because of the greater proportion of carbon monoxid it contains. The analysis of samples of these gaseous mixtures gave the results recorded in the following table :

COMPOSITION OF ILLUMINATING GASES

Constituents	Old Process	Water Gas
Hydrogen	49.0 %	32.1 %
Methane	34.5	20.0
Ethylene (and other hydrocarbons)	6.0	12.5
Carbon monoxid	7.0	30.0
Carbon dioxid	1.1	2.6
Nitrogen	3.5	2.0
Ammonia	trace	trace
Hydrogen sulfid	trace	trace

NATURAL GAS. In numerous localities underground accumulations of combustible gases have been found. When a "gas well" is bored, these gases rush out with great force, and the pressure they are under is often sufficient to force them in pipes through long distances.

SOME COMMON LIQUID AND SOLID HYDROCARBONS. Since 1860, petroleum or rock-oil and its products have come into very general use. The crude product is usually obtained by boring wells. The great petroleum producing regions are Pennsylvania, Texas, Baku (Russia), and the Rangoon district in Burma.

Petroleum is a mixture of substances, the majority of which are hydrocarbons. The crude oil is refined by successive treatment, first with sulfuric acid, then with caustic potash, and is finally fractionally distilled, *i. e.*, it is distilled, and the distillates that come over between certain temperatures are collected separately. The most volatile product, *rhigolene*, boils at about 18°. This evaporates so readily at ordinary temperatures that it produces great cold, and is hence used as a refrigerant. *Gasoline* boils at about 49°, and is extensively used as a fuel, and in "gasoline engines" and lamps. Several grades of naphthas boiling from 50° to 150° are separated and used for dissolving resins and oils in various manufactures and as fuel. The commercial names given to these light oils are *benzine, petroleum ether*, and *ligroin*. The product boiling between 150° and 250° is *kerosene*, which is extensively used in lamps. Other illuminating oils similar to kerosene are *photogene, solar oil*, and *paraffin oil*. These form more than half of the petroleum. The mineral or paraffin lubricating oils boil above kerosene, and are used to lubricate machinery. *Paraffin* is the last commercial product; it is a white, waxy solid, melting at about 58°, and is used in making candles, and in other ways.

Exercises

1. How are the Laws of Definite Proportions and Multiple Proportions by Volume illustrated by the facts revealed by the combustion of methane, ethylene, and acetylene?

2. Given a mixture of equal volumes of methane and carbon dioxid, how would you separate the gases?

3. Given a compound supposed to contain carbon and hydrogen, how would you prove the presence of these elements?

Problems

1. If 6 *l.* of a mixture of equal volumes of methane and ethylene are burned, how many liters of gas and what gases are formed?

2. If 683 *c. c.* of water vapor is passed over incandescent coke, and 80 per cent of it dissociated, what are the respective volumes of the products under the same conditions of temperature and pressure as the water vapor?

JUSTUS VON LIEBIG

1803-1873; German

Active in organic and agricultural chemistry. Invented condenser bearing his name, and perfected methods of analyzing compounds of carbon

ROBERT W. BUNSEN

1811-1899; German

Invented the burner, photometer, and battery bearing his name. Invented with Kirchhoff the spectroscope, and by its aid discovered rubidium and caesium

JOHANN JACOBUS BERZELIUS

1799-1848; Swede

Fixed many equivalent weights. Introduced present-day chemical symbols. Influence as a teacher very marked. Proposed the dualistic and the electrochemical theory

EILHARD MITSCHERLICH

1794-1863; German

Devised a method of estimating atomic weights of elements from the shape of the crystals of their compounds

FRIEDRICH WÖHLER

1800-1882; German

Discovered aluminum and beryllium. Removed the barrier between organic and inorganic chemistry

Plate IV

BUNSEN

LIEBIG

BERZELIUS

WÖHLER

MITSCHERLICH

Plate IV

THE ATMOSPHERE

110. Density and Use. The earth is surrounded by a gaseous envelope called the *atmosphere*. A limited portion of it is usually called *air*. The density of air decreases with the altitude and it has been computed that at altitudes of 100 miles the density is less than that in the best vacuums which man has as yet obtained. The atmosphere not only moderates the heat of the sun, but is also a protection against the cold of interstellar space. In it float the clouds formed from water vapor ascending from earth and sea, and in it are suspended dust, smoke, etc. The weight of the air pressing upon the earth's surface amounts to about fifteen pounds to the square inch, and will balance a column of mercury 76 $^{cm.}$ high (page 15).

HISTORICAL NOTE. Air was regarded as an element before the eighteenth century, and all gaseous substances were supposed to be but different kinds of air. The demonstration that air is not an element but is a mixture of various gases marks the debut of modern chemistry. This fact was first brought to light in 1775 by Lavoisier in France and almost simultaneously by Scheele in Sweden.

Lavoisier heated mercury to its boiling point in a confined volume of air; the mercury combined with the oxygen, leaving the nitrogen. His apparatus is shown in Fig. 21. *MMN* is the furnace heating the flask whose curved neck opens under a jar placed over a vessel of mercury. Mercury was placed in the flask and

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the neck filled with mercury from the vessel up to L; a certain definite volume of air was thus confined above the mercury in the flask and that in the neck. The mercury in the flask was kept gently boiling for twelve days. The air was then found to have shrunk in volume from fifty cubic inches to forty-two cubic inches. The red powder (oxid of mercury) that appeared on the surface of the mercury was carefully collected and then heated to a higher temperature; it gave off eight cubic inches of "air eminently respirable," or oxygen, as Lavoisier called it. The gas left in the flask was mainly nitrogen. Lavoisier concluded that air is composed of about four volumes of nitrogen and one volume of oxygen, and on mixing these gases in this ratio, he obtained an air very similar to that of the atmosphere.
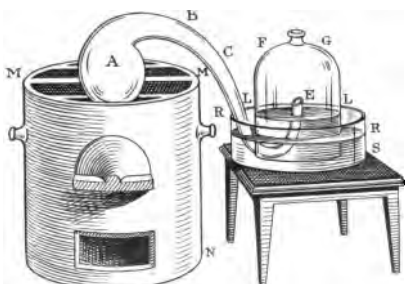
Fig. 21 — LAVOISIER'S APPARATUS FOR DETERMINING THE PROPORTION OF OXYGEN IN THE AIR

Scheele absorbed the oxygen of the air by means of certain solutions (alkalin sulfids); his analysis, however, was less accurate than that of Lavoisier.

·III. **Liquid Air.** Air was first liquefied in 1877, but in very small amounts. In the last few years, however, methods have been devised for obtaining large amounts of liquid air with comparative cheapness. This liquid air can be kept for some time in vessels known as Dewar's bulbs (Fig. 22). These consist of two flasks or tubes sealed together at their tops, and the space between them made as perfect a vacuum as possible. A vacuum is so poor a conductor of heat that the liquid air can be shipped long distances without any great amount of evaporation.

The intense cold readily obtainable by the aid of liquid air permits of the performance of many striking experiments. But few practical applications of liquid air have as yet been developed.

112. Composition. Besides nitrogen, argon, and oxygen, and very minute amounts of hydrogen and helium and other gases, air contains water vapor and carbon dioxid; and in very small proportions and in restricted amounts, ammonia, ozone, dust, living and dead

Fig. 22 — DEWAR BULB

germs. The first three elements may be termed permanent constituents, as their proportion varies but little, no matter what the source of the air; the other constituents vary considerably. The results of many experiments on air derived from all parts of the earth have shown that air contains about 21 per cent of oxygen (by volume), 78 per cent of nitrogen, and 1 per cent of argon and other constituents.

Water is a most variable constituent. In cold and in desert places the air is almost destitute of water; in warm and wet weather and in most torrid climates it contains much more. A good deal of water vapor in the atmosphere, *i. e.* a high degree of humidity, checks the evaporation of perspiration from the skin, causing a sticky and uncomfortable feeling, while in dry, warm air evaporation takes place so rapidly that the skin becomes feverish and the mouth parched. Carbon dioxid is also quite

variable in quantity; on an average, air contains
0.04 per cent. In crowded rooms, especially if
heated by lamps or gas, the amount may run as
high as 0.3 per cent. If more than 0.1 per cent is
present the air should be regarded as too impure
to be fit for respiration.

NOTE. It has been shown that hydrogen is a normal constit-
uent of the air to the extent of about 0.02 per cent. As there are
numerous processes in nature by which hydrogen is set free, it is
believed that an increase in the amount of hydrogen in the air is
prevented by its gradually working its way, because of its rapidity
of diffusion, to the outer limits of the atmosphere and escaping
into stellar space.

113. Air Not a Compound. That air is not a
compound, but merely a mixture, is proved by the
following facts:

1. If air be dissolved in water and the dissolved
air analyzed, it is found that it contains a little less
than two volumes of nitrogen to one of oxygen.
The oxygen is more soluble than the nitrogen, and
hence is present in greater proportion in the solu-
tion.

2. When liquid air boils, the nitrogen passes off
more rapidly than the oxygen, so that the residual
liquid becomes richer and richer in oxygen (page 28).

3. When four volumes of nitrogen are mixed
with one of oxygen, the resulting mixture has all
the properties of ordinary air, and yet the mixing
is accomplished without any liberation or absorp-
tion of heat or change of volume, as would be the
case in a chemical union of the two gases (§14, *2*).

4. When air is passed through porous sub-
stances, a partial separation of the oxygen and

nitrogen occurs, because they have different rates of transpiration (page 35).

5. Its carbon dioxid may be separated by liquefying the air and filtering off the solidified carbon dioxid.

6. Its water may be removed by cooling the air below o°.

7. Dust and other suspended particles may be removed by filtering the air through cotton batting.

All of the above processes are of a physical nature, and as a separation of the constituents of the atmosphere can be effected by their aid, air cannot be a compound.

Perhaps the strongest proof that air is not a compound is the fact that the percentage of oxygen it contains is variable; some samples of air contain more than half a per cent less than what is considered normal (§14, *3*).

114. Solid Matter in the Air. When sunlight is admitted into a dark room through a chink in the shutter, it streams across the room as a beam of light in which motes may be seen dancing about. If the dust on the floor of the room be stirred up, the beam of light appears more brilliant. If a beam of light be sent through a long and wide glass tube smeared on the inside with glycerin, it at first appears brilliant, but as the dust is caught and held by the sticky glycerin, it loses its brilliance and finally becomes invisible.

These observations show that air is ordinarily more or less filled with solid particles. These particles are of quite various nature. In the vicinity of the sea, salt particles abound, because the spray

of the sea is caught by the wind, the water evaporated, and the particles of salt which were dissolved in it are carried about in the air. In cities and manufacturing districts, smoke particles are numerous. These particles play an important part in the formation of rain and fog. It can be shown that air deprived of its solid particles by filtering it through cotton wool, cannot form droplets even though it be saturated with water vapor. These solid particles seem to act as points or nuclei upon which the moisture deposits in liquid form. The organic impurities, the bacteria, germs, etc., which are present in countless numbers in ordinary air also play an important part in the fermentation and putrefaction of plants and animals, and in the communication of disease. The breathing of the same air over and over again, as in crowded halls or theaters, produces headache, not so much because of the diminution of the oxygen and the increase of the carbon dioxid as because of the organic impurities evolved during respiration. The unpleasant smell noticed on entering poorly ventilated rooms filled with people is also due to the same cause.

115. Air and Life. Each of the constituents of the atmosphere has its peculiar part to play in the existing order of things. Animal life requires oxygen for its continuance, and vegetable life, carbon dioxid. Animals take in oxygen and give out carbon dioxid; plants take in carbon dioxid and give out oxygen. A nice balance between the two gases must be preserved in the atmosphere, else life perishes. Nitrogen serves to dilute oxygen, so that the chemical activity of the latter may be

restrained. With an atmosphere of nitrogen alone, life would be impossible; with one of oxygen, animal life would be so intense that it would soon cease, while combustion once started would proceed with uncontrollable rapidity. Water as cloud and rain also has its part to play, and ammonia and nitric acid help in the fertilization of the soil.

Exercises

1. In what ways is diffusion illustrated by the atmosphere?

2. What chemical changes are produced in the air by the action of lightning?

3. In what respects does " atmospheric nitrogen " differ from nitrogen obtained from a compound?

Problems

1. What volumes of gases will be left after 6 *l.* of methane and 4 *l.* of air are made to unite as far as possible?

2. A mixture of 12.5 *c. c.* of air and 25 *c. c.* of hydrogen was exploded, and the residual gas found to measure 30.2 *c. c.* What per cent of oxygen did the air contain?

3. Dumas and Boussingault in 1841 found 16.053 *g.* of air to contain 3.18 *g.* of oxygen. What per cent of oxygen is this?

4. If air on an average contains 23 per cent by weight of oxygen, what is the per cent by volume of the oxygen in it?

5. 10 *l.* of air are passed through a tube partially filled with red-hot copper, and an increase in its weight of 2.97 *g.* was observed. What per cent of oxygen by weight is contained in the air?

6. How much oxygen and nitrogen expressed in percentages by weight does a sample of air contain, which, according to Bunsen, was made up of 20.96 per cent of oxygen and 79.04 per cent of nitrogen expressed in percentages by volume?

7. (*a*) How many liters of air are there in a room 3 *m.* high, 5 *m.* long, and 4 *m.* wide? (*b*) How many liters of oxygen at 0° and 760 *mm.* does it contain? (*c*) How many grams of burning charcoal will completely consume it if it burns to carbon dioxid? (*d*) How many grams of burning charcoal will contaminate the air with 5 per cent of carbon dioxid?

FIRE AND FLAME

116. The Source of Heat and Power. The chemical union of carbon or hydrogen with oxygen is of the greatest practical importance, as being the source of most of our heat and power. All fuels contain large proportions of carbon or hydrogen, or of both elements, and their union with the oxygen of the air gives out large amounts of heat. This heat may be utilized to warm and light our dwellings, cook our food, drive our steam engines, and do a host of other things. The equivalent of the heat energy is pent up, so to speak, in the fuel and may be preserved and transported from place to place so as to be available whenever and wherever it may be desired. Carbon, hydrogen, and their compounds are not, indeed, the only substances whose union with oxygen is accompanied with the evolution of much heat and light, but so important is the burning of these two elements, free or in combination, that its consideration demands special attention.

117. Combustion. Combustion is the technical name for burning. It signifies a rapid combination with oxygen. To express less rapid combination with oxygen, as in respiration and decay, the expression *slow combustion* is employed. The amount of heat given out during a combustion depends

mainly upon the nature of the combustible, while the amount of light usually depends upon the presence of solid particles in the products of the combustion and the rapidity of the combustion. A piece of wood may burn up in a few minutes or may decay through ages, but in both cases the same amount of heat is given out and the products are the same, *viz*, water, carbon dioxid, and ash.

118. Kindling Temperature. It is a common experience that different substances have to be heated to different temperatures before they will take fire and burn. Thus, hard coal has to be raised to a higher temperature than soft coal before it will catch fire, and other cases readily present themselves. The lowest temperature at which a substance takes fire and burns is called its *kindling temperature* or *point of ignition*.

If a piece of wire gauze is brought down over a flame, it conducts the heat away so rapidly that the gas which may escape through the gauze is cooled below its kindling point and hence does not catch fire. Also if a flame is enclosed in an envelope of wire gauze and brought into a gaseous mixture which would explode if its temperature were sufficiently raised, no explosion ensues, as the gauze mantle distributes and dissipates the heat so that the mixture outside is not raised to its ignition temperature. The explosive mixture indeed enters the gauze envelope and burns quietly therein, but the mixture outside does not take fire.

Prior to 1810 explosions in coal mines were very frequent; the explosive mixture was composed of methane (fire damp) and air, but when Davy

invented his "safety lamp" (Fig. 23), such explosions became impossible, provided the miner kept his lamp in good working condition.

Fig. 23 — DAVY "SAFETY LAMP"
The gauze distributes the heat so that the explosive gases outside are not ignited

119. Flame. Some substances, in burning, merely glow, as charcoal and punk; others exhibit the phenomenon of flame. In the first case the combustibles are solids which burn directly, *i. e.*, do not decompose into other substances of a liquid or gaseous nature; while in the second case, the combustible is either a vaporizable solid or liquid, or a gas, or decomposes into vapors or gases which then burn. A flame is composed of the hot gases or vapors formed during or previous to the combustion.

120. Combustible and Supporter of Combustion. It is customary to consider one of the substances taking part in a combustion as the combustible, and the other as the supporter of the combustion; the latter generally surrounds or envelops the former. In all the more familiar cases of combustion the air, or rather the oxygen it contains, is regarded as the supporter of combustion, and in ordinary language the terms combustible and non-combustible are applied to substances which burn or do not burn in air. Also it has become customary to consider other gases as supporters or non-supporters of combustion when they behave toward a combustible as air does. These distinctions, though convenient, are purely

arbitrary, as may be illustrated in the following manner:

A large lamp chimney is fitted at its lower end with a two-hole cork through which is passed a straight tube of rather wide bore and a longer tube (Fig. 24). Illumi-nating gas is passed into the chimney through the longer tube and ignited at the top, over which is placed a piece of wire gauze. This creates a draft up through the wide straight tube, and the air which passes into the chim-ney may be ignited by push-ing a lighted taper up the tube. We then have the spectacle of a gas burning in air and of air burning in gas. It is evident that there is nothing in the nature of the substances to determine which is to be regarded as the combustible and which as the supporter of combustion. Furthermore, since the ex-perimental conditions determine which of the two sub-stances surrounds the other, it is seen that the terms com-bustible and non-combusti-

Fig. 24 — APPARATUS FOR SHOWING GAS BURNING IN AIR AND AIR BURN-ING IN GAS

ble, as applied to chemical substances, do not express any definite property of those substances.

121. Spontaneous Combustion. It is by no means a rare occurrence that conflagrations are caused by heaps of combustible substances, espe-cially oil-soaked rags which have been used in cleaning machinery, taking fire of themselves. Usually in such cases reactions take place so rap-idly that the heat thereby generated is sufficient to

ignite the entire mass. Such burning is said to be due to spontaneous combustion.

122. Luminosity of Flame. A flame is rendered luminous commonly when it contains solid particles which may be heated to incandescence. The flame of burning hydrogen gives out almost no light because neither the reacting substances nor the product of combustion (water) contain any solid matter. The same is true of an alcohol flame, where the products of combustion are water and carbon dioxid. Such flames may be rendered luminous by sifting fine powders, as fine sand or powdered charcoal, into them. Each solid particle becomes heated to incandescence and thus acts as a source of light. The flame of lighted magnesium is brilliant because the solid particles of magnesium oxid produced become white hot. The flames of wood, candles, and similar substances are bright because they contain incandescent particles of soot or carbon. The oxyhydrogen flame can be made very bright by mixing the vapor of benzine with the hydrogen; benzine contains the carbon to furnish the necessary solid particles to produce luminosity.

Luminous flames may also be produced, even when no solid particles are present; thus an increase in the density of combining gases also renders the flame luminous. Highly compressed oxygen and hydrogen may be made to give a very bright flame.

123. Structure of Flame. All common flames have an essentially similar structure. Three separate cone-shaped envelopes may be distinguished, which are most easily seen by catching on white

paper the shadow of the flame placed in bright sunlight. The Bunsen flame is an example of a non-luminous flame. The interior cone is of a greenish color and gives no light; the intermediate one is pale blue, and the exterior a dark blue. The candle flame is an example of a luminous flame. The interior cone is almost black; the intermediate, yellow and luminous, while the exterior is hardly discernible except at the base, where it is dark blue. (Fig. 25.)

The flames of gases giving but one product of combustion contain only one combustion zone. Thus, the flames of hydrogen and of carbon monoxid, whose products are water and carbon dioxid, respectively, exhibit only one zone.

124. Combustion in a Candle Flame. The wax, tallow, or paraffin of which candles are made consist of substances containing much carbon and hydrogen. When the wick is lighted, the heat melts the wax, and the liquid is drawn up the wick by capillary attraction. It there vaporizes and its vapor diffuses toward the outer portions of the flame (Fig. 25). The oxygen of the air diffuses into the exterior and the intermediate cones where the temperature is high enough to cause combustion. The oxygen does not enter the inner cone. In the middle cone the combustion of the carbon is not total, so that the incandescent particles there emit light; these are burned up in the outer cone. When the supply of air is insufficient or when there is a strong draft, the candle smokes, *i. e.*, gives off unburned carbon.

Fig. 25. STRUCTURE OF CANDLE FLAME

125. Smoke. Smoke consists mainly of particles of unconsumed combustible (carbon in the form of soot) mingled with the gaseous products of the combustion. The up-rushing hot gases carry the unburned particles out of the chimney, and as the gases mix with the air and become cooled off, the particles fall to the ground. Smoke is not only a nuisance, but is also a direct loss, for each particle of unburned carbon that escapes up the chimney represents a certain amount of heat gone to waste.

Smoke Consumers. Smoke consumers are contrivances to prevent the escape into the air of any unburned combustible. They do this by bringing the unconsumed particles to a high temperature in contact with an abundant supply of oxygen, whereby complete combustion is insured. Smoke consumers not only render the atmosphere in the vicinity of places where much coal is used more healthful and agreeable, but are also a saving to the user.

126. Temperature of Flames. If in the oxyhydrogen flame all the heat of combination were used in raising the temperature of the water formed, a temperature of about 6,800° would be attained. In reality, however, the temperature has been found to be much lower, *viz.*, 2,800°. The reason is that the union is not complete, and hence the calculated value (6,800°) is too large. It has been observed that at temperatures above 1,000°, water vapor dissociates partially into its elements (page 60). Hydrogen and oxygen at temperatures above 1,000° do not unite completely to form water; the higher the temperature, the smaller the amount of water vapor formed, and therefore the less the heat of combination. When hydrogen burns, the great

heat evolved dissociates the water partially, and as this requires heat, the temperature is lowered. Such is the state of affairs with most flames; the products of combustion are dissociated, thus lowering the temperature.

127. Speed of Propagation of Flame. If any part of a mixture of gases which are in the right proportions to combine and whose union is exothermic (page 58), be heated to the proper temperature, combination ensues and spreads through the mixture at a speed depending upon the nature of the gases. If a mixture is combustible (illuminating gas and air) and is issuing from a tube at whose orifice it may be ignited, three cases are possible:

1. If the speed of flow from the tube is greater than the speed of propagation of the flame of the mixture, it cannot be ignited.

2. If the speed of flow is less than that of the propagation of the flame, the gas may be ignited and the flame will pass back through the tube.

3. If the speed of flow is about the same as the speed of propagation the flame will remain at the mouth of the tube.

The "blowing out" of a flame can be accomplished only when the speed of the draft of air exceeds the speed of propagation of the flame, although the cooling effect of the draft has some influence.

128. Combustion in a Bunsen Flame. A Bunsen burner (Fig. 26) consists essentially of a tube, at the base of which illuminating gas enters through a fine orifice, *m*. Just above the orifice are openings

of adjustable size in the tube, *a*. The gas on escaping from the fine orifice draws in air from the "air holes." The two gases mix in the tube and when their proportions are properly adjusted, give a non-luminous flame. If the speed of flow of the gas is made less by cutting off the gas supply somewhat, or if the speed of propagation of the flame is increased by heating the tube or supplying more air, the flame finally passes back into the burner, producing the phenomenon known as "striking back."
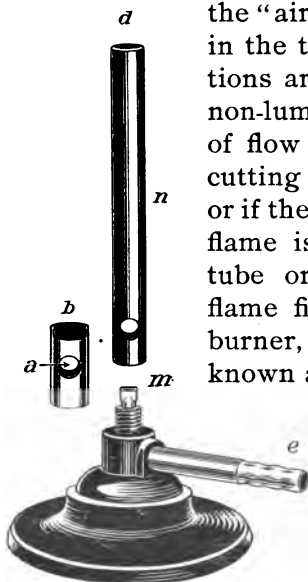
Fig. 26 — BUNSEN BURNER

THE INCANDESCENT GAS BURNER. The Bunsen flame is extensively used in producing the so-called "Welsbach light." The non-luminous flame is surrounded by a "mantle" composed of a mixture of the oxids of certain rare metals which it heats to a high temperature, thus causing the mantle to give out a more intense and steady light than the ordinary gas jet.

129. Explosions. Explosions are caused when rapid chemical combination takes place between substances yielding gaseous products. The heat accompanying the reaction raises the temperature of the gases so that they occupy a far greater volume, and this sudden expansion calls into action an enormous pressure. An explosion is never instantaneous. It takes a certain, although very small, interval of time for the reaction to spread

through the exploding mass. By confining the explosive in one end of a long tube and starting the reaction, a measurable interval of time elapses before the explosive wave reaches the other end.

Explosions have sometimes occurred in flour mills and starch factories, due to the air in them being filled with a dust of very fine flour or starch, and this mixture coming in contact with a flame. The ignition of the combustible dust started at one point flashes through the whole mixture. The result is that a large volume of the gaseous products of combustion, carbon dioxid and water vapor, is suddenly generated, causing an explosion.

MODES OF ATTAINING HIGH TEMPERATURES. There are three principal modes of raising the temperature of a substance — (*1*) by the concentration of the sun's rays; (*2*) by combustion; (*3*) by the electric furnace.

1. The sun's rays may be concentrated — brought to a focus — by means of "burning glasses" (double convex lens) or properly placed mirrors. Although the temperature can be raised very high if large lenses or many mirrors are used, the method cannot be applied except to rather small bodies. The utilization of the sun's rays as a source of power in the treeless plains of the West is still in the experimental stage. It has its advantages, however, and it was the source of heat employed by Priestley which led to the discovery of oxygen (page 26); also by Lavoisier in his investigation of the combustibility of diamond.

2. The commonest method of getting high temperatures is by means of the combustion of fuel. Many different modes of doing this most effectively for the purpose in hand have been devised. Besides the forms of furnaces which are familiar to every one, there are three other general types which are much used in the extraction of metals from their ores.

In the *muffle furnace* (Fig. 27) the substance to be heated, the *charge*, is enclosed in a fire-clay box or retort which is placed over the fire so that neither the fuel nor the fire gases can enter it.

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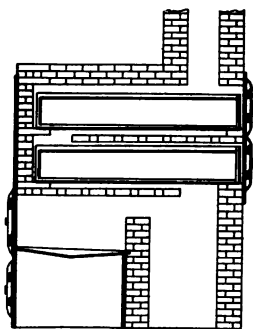
Fig. 27—A MUFFLE FURNACE

In the *reverberatory furnace* (Fig. 28) the charge is placed on the bed of the furnace, the roof of which is given a slope so that the flames and gases from the fire in the grate are deflected down upon it. The substance is spread out in a thin layer on the bed and may be oxidized or reduced according to the method of firing and the proportion of air admitted.

3. *Shaft furnaces* or kilns are either *periodic* or *continuous.* After the heating of a charge in a periodic furnace, it is allowed to cool before it is emptied and recharged. In the continuous furnace, however, the heated material is withdrawn and a fresh charge added without loss of time or waste of heat. In some forms of continuous furnaces fuel and material are added in alternate layers, while in others the fuel is burned on a separate grate and only the gaseous products of the combustion come in contact with the charge in the shaft. The construction and operation of the form of a shaft furnace known as a *blast furnace* is given under Iron.
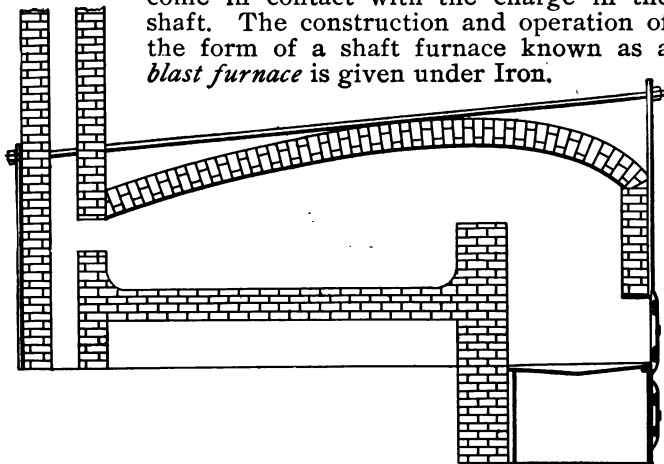
Fig. 28 — A REVERBERATORY FURNACE

4. Electric furnaces (Fig. 29) consist essentially of a receptacle of infusible material in which the charge is placed, and electrodes passing through the furnace walls. The arc formed on the passing of the current is a center of intense heat which is communicated to the charge. In certain forms of the electric furnace (Fig. 30) the charge itself is made to carry the current, and, as the materials of which it is composed offer great resistance to the passage of the current, the charge is heated to a very high temperature.
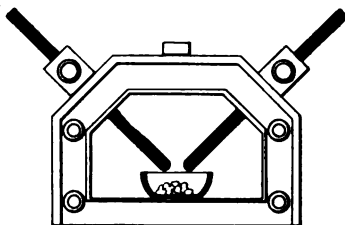
Fig. 29 — AN ELECTRIC FURNACE

The introduction of the electrical furnace into practical operations has revolutionized some industries and created others. At the temperatures obtainable by its use reactions are made to occur between substances which at the highest temperature obtained in combustion furnaces are chemically inert toward each other. Several new and important products, such as calcium carbid and carborundum, have been recently thrown upon the market, the manufacture of which has been made possible only by the aid of the electric furnace.
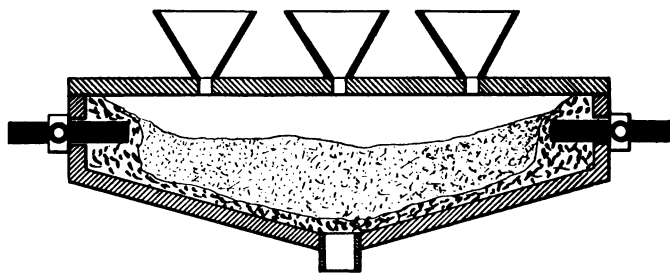
Fig. 30—A RESISTANCE FURNACE

The center of the electro-chemical industry of this country is at Niagara Falls, where large supplies of electricity are available at a reasonable cost.

130. Oxidizing and Reducing Flames; The Blowpipe. The outer area of a flame contains an excess of oxygen, while the inner region, where there is unburnt hydrogen or hydrocarbons, has a deficiency of oxygen. An oxidizable substance placed in the outer cone is converted into an oxid, while in the inner cone many oxids are reduced. In practice these different actions of the two parts of a flame are utilized by means of a blowpipe. This instrument consists essentially of a tube ending in a fine jet (Fig. 31). For convenience of manipulation the jet tube is usually placed at right angles to the main part of the tube. If the orifice of the jet be placed just outside the middle part of the flame and air be forced through it from the lungs or a bellows, the oxidizing flame is produced and may be directed upon a substance held in a convenient support. When the orifice is placed in the middle of a flame its reducing part may be blown on a substance.

Fig. 31—
BLOW-
PIPE

THE PHLOGISTON THEORY. The phenomena of combustion are so striking and important that attempts were early made to find a theoretical explanation of it. One of these theories, suggested by Becher and developed by Stahl, was dominant for over a century. The theory was based upon the hypothesis that a certain substance called phlogiston is present in every combustible, and that when combustion occurs, this substance passes off. Easily combustible substances, such as charcoal and oils, were supposed to be very rich in phlogiston, while incombustible substances contained none. When metals burned or rusted, they were said to lose phlogiston, which could be restored to them by heating with charcoal. Oxidation, then, was the result of a loss, and reduction, of a gain of phlogiston.

According to this theory, metals were compounds of phlogiston and their "calxes," as oxids were then called. The fact that the calxes were heavier than the metals themselves was explained away by assuming that phlogiston possessed a sort of negative gravity, for, said the chemists of that period, when wood burns, its smoke ascends and does not seek the earth as heavy bodies should.

This theory may, in the light of our present knowledge, seem absurd, but it must not be forgotten that it was believed in and upheld by many chemists for more than a century. That it was valuable and useful, there can be no doubt, for it introduced a certain law and order into chemistry which led to the discovery of many important facts. It was given up only when the part that oxygen plays in combustion was made clear by Lavoisier in 1783.

Exercises

1. What makes a lamp smoke?

2. Why have large lamps a powerful central draft?

3. Why is a candle flame tapering and conical?

4. Explain how a flame is "blown out."

5. Why is it that a mixture of a gaseous hydrocarbon with air or oxygen will explode, although the gas alone will burn quietly?

6. What relation is there between the light of an ignited substance and its temperature?

7. Why does a moderate blast of air help combustion, while a strong one may hinder and even stop it?

8. Why is the temperature and consumption of fuel reduced by closing the drafts of a furnace?

9. What are the valuable constituents of ordinary combustibles?

10. Which of the gases thus far studied, when burned, give out the most light? The least?

COMBINING AND ELEMENTAL WEIGHTS

SYMBOLS, FORMULAS, AND EQUATIONS

131. Combining Weights. We have learned that elements enter into combination according to definite proportions, both by weight and by volume. Thus, any sample of pure water always consists of 11.19 per cent of hydrogen and 88.81 per cent of oxygen. The ratio of these numbers is approximately 2 : 16. For hydrogen dioxid the ratio is about 2 : (2 × 16). Likewise ratios were found for all the elements thus far studied. The constantly recurring numbers, 16 for oxygen, 14 for nitrogen, 12 for carbon, and 1 for hydrogen, stand for the relative weights of these elements which enter into combination; they are called the *combining weights* of the elements. Every element has a combining weight which is as characteristic of it as its color, density, or any other property. These weights depend for their numerical values only upon what units of volume and mass are adopted.

132. Elemental Weights. In the following table are given the weights of a liter of most of the gases thus far studied, together with the weights of the elements contained in a liter of their gaseous compounds.

TABLE OF WEIGHTS

GAS	Weight in grams of one liter	Weight in grams of hydrogen in one liter of gas	Weight in grams of carbon in one liter of gas	Weight in grams of nitrogen in one liter of gas	Weight in grams of oxygen in one liter of gas
Hydrogen	0.090	2 × 0.045	--	--	--
Oxygen	1.430	--	--	--	2 × 0.715
Nitrogen	1.250	--	--	2 × 0.625	--
Ammonia	0.760	3 × 0.045	--	0.625	--
Steam	0.805	2 × 0.045	--	--	0.715
Carbon dioxid	1.966	--	0.536	--	2 × 0.715
Carbon monoxid	1.251	--	0.536	--	0.715
Cyanogen	2.322	--	2 × 0.536	2 × 0.625	--
Hydrazoic acid	1.920	0.045	--	3 × 0.625	--
Methane	0.716	4 × 0.045	0.536	--	--
Ethylene	1.252	4 × 0.045	2 × 0.536	--	--
Acetylene	1.162	2 × 0.045	2 × 0.536	--	--

The table shows that the weights of hydrogen, carbon, nitrogen, and oxygen contained in a liter of any of their gaseous compounds are 0.045 $g.$, 0.536 $g.$, 0.625 $g.$, and 0.715 $g.$, respectively, or some multiple of these weights. These weights represent the combining proportions of these elements referred to one liter of their gaseous compounds, and may be called *elemental weights.*

The elemental weight of an element is the smallest weight of it in grams contained in a liter of any of its gaseous compounds.

Since the choice of a liter as the common volume is arbitrary, any other volume may be taken, if there be sufficient reason for so doing. If the volume of 22.2 $l.$ be taken, the elemental weights, which are rather inconvenient decimal fractions, become changed into the combining weights, which are approximately integral numbers. Thus, by multiplying the elemental weights by 22.2, we get, on

neglecting the small fractional parts, the integral number of grams of the elements contained in 22.2^l of the gaseous compounds.

$0.045 \times 22.2 =$ (*very nearly*) 1, the combining weight of hydrogen.
$0.536 \times 22.2 =$ "   "   12, "   "   "   " carbon.
$0.625 \times 22.2 =$ "   "   14, "   "   "   " nitrogen.
$0.715 \times 22.2 =$ "   "   16, "   "   "   " oxygen.

NOTE. The student ought perhaps to be told before he goes further that the combining weights are very seldom integral. Thus, a series of very careful analyses and syntheses of water has proved that if the combining weight of hydrogen be taken as unity, that of oxygen is 15.879. For all that, the combining weights are, with but few exceptions, so close to being integral, that the nearest integer may be taken for most cases. By so doing, the mind is not confused by retaining inconvenient numbers in memory. The system of elemental weights also suffers under the disadvantage of consisting of inconvenient numbers, and as soon as it has served its purpose it will be dropped.

An important fact brought out by the table is that the weight of a liter of hydrogen, of nitrogen, or of oxygen in the free state is double its elemental weight.

133. Symbols. Symbols are shorthand expressions of facts which facilitate greatly the study of a science, for, by their use, statements which, put in words, can be grasped only with difficulty, are rendered much more easy to handle. We have thus far perhaps not felt their want because the number of substances studied has been limited. From now on, however, we shall make free use of them.

In the choice of symbols two points should be observed: *The symbols must be as simple as possible; they must be as comprehensive as possible.*

As symbols of the chemical elements the initial letters of their names are taken, and in case two or

more elements have names commencing with the same letter, another letter in the name is added. The symbol of hydrogen is, accordingly, H; that of carbon, C; that of nitrogen, N; and that of oxygen, O; while the symbol of helium is He; that of cadmium, Cd; that of calcium, Ca; that of nickel, Ni; that of osmium, Os.

In some cases the symbols are derived from words not in the English language. Thus, the German words for sodium and for potassium are *Natrium* and *Kalium*, which in turn are of Arabic origin, whence the symbols Na and K. The symbols for silver, iron, and lead are Ag, Fe, and Pb, derived from the Latin words *argentum*, *ferrum*, and *plumbum*. It is to be noted that when a symbol is composed of two letters the first is always a capital and the second a small letter.

Symbols also denote definite quantities of their respective elements. Thus, if hydrogen be taken as unity, then H denotes a unit weight (one gram, one pound, one ton, etc.) and C, N, and O denote a weight 12, 14, and 16 times this unit weight, respectively. If the symbol H be taken to stand for the smallest weight in grams of hydrogen contained in a liter of any of its gaseous compounds, then C, N, and O represent the smallest weights in grams, *viz.*, 0.536^g, 0.625^g, and 0.715^g, respectively, that can exist in a liter of any of their gaseous compounds. H, C, N, and O may represent the combining weights, the elemental weights, or any other corresponding set of weights, for such sets of weights are ratios and depend for their value only upon what weight is taken as a standard.

134. Formulas. By writing the symbols composing a compound one after another and by indicating with a subscript (also called sub-figure) the number of times a symbol occurs, the formula of a compound is obtained. The order in which the symbols is written is immaterial, although there is usually some customary or preferred order. The subscript refers only to the symbol under which it is written. Often two or more symbols are written in parentheses with a subscript, the subscript then referring to all the symbols within the parentheses. Thus, the formulas, CaO_2H_2 and $Ca(OH)_2$ stand for the same compound, calcium hydroxid; the second mode of expression is preferred for reasons given below. When a number is written before a formula, it has the same effect as a coefficient in algebra, and multiplies all the symbols in the formula. Thus, $5 Ca(OH)_2$ indicates five symbols of calcium and ten each of oxygen and hydrogen.

135. Radicals. There are many groups of elements which seem to hold together in most chemical reactions, but which cannot be isolated as a definite compound. Such groups are called *radicals.* Thus, the OH in the formula $Ca(OH)_2$ is an important radical named *hydroxyl,* a word recalling the elements of which it is composed — *hydro,* an abbreviation of hydrogen, and *oxyl,* one of oxygen. Another important radical is *ammonium,* NH_4. The formula for ammonium hydroxid is written NH_4OH and not NH_5O, so as to emphasize the fact that it consists of the radicals, ammonium and hydroxyl. When a radical occurs more than once in a formula it is usually enclosed in parenthesis; for example,

$Ca(OH)_2$, calcium hydroxid, and ammonium carbonate, $(NH_4)_2CO_3$.

136. Formulas; Combining and Elemental Weights. When the weights of the constituent elements in a definite volume of a gaseous compound are known, the formula of the compound can be readily established. To illustrate, one liter of ammonia contains 0.625 $g.$ of nitrogen and 3×0.045 $g.$ of hydrogen. (Cf. table, § 132.) It contains one elemental weight of nitrogen and three of hydrogen, and inasmuch as the symbols stand for these elemental weights, the formula of ammonia is seen to be NH_3. One liter of methane contains 0.536 $g.$ of carbon and 4×0.045 $g.$ of hydrogen; its formula is therefore CH_4. In a liter of water vapor there are 0.715 $g.$ of oxygen and 2×0.045 $g.$ of hydrogen, and its formula is H_2O. One liter of carbon monoxid contains 0.536 $g.$ of carbon and 0.715 $g.$ of oxygen, and one liter of carbon dioxid contains 0.536 $g.$ of carbon and 2×0.715 $g.$ of oxygen; hence their formulas are CO and CO_2, respectively.

Similarly, formulas for the free elements may be found. A liter of hydrogen weighs 2×0.045 $g.$, so that its formula is H_2. The formulas for free nitrogen and oxygen are N_2 and O_2, respectively, since a liter of either gas weighs twice as much as the smallest weight of it in grams contained in a liter of any of its gaseous compounds. Also, by indirect methods, the weight of a liter of ozone has been estimated to be 3×0.715 $g.$, making its formula O_3.

In like manner the formula of a compound may be established by considering the combining weights, *i. e.*, the weights in grams of the elements

contained in 22.2 ^{l} of the compound. 22.2 ^{l} of ethylene contain 2 × 12 ^{g} of carbon and 4 × 1 ^{g} of hydrogen; hence its formula is C_2H_4. The formula of acetylene is C_2H_2, because 22.2 ^{l} of it are made up of 2 × 12 ^{g} of carbon and 2 × 1 ^{g} of hydrogen. 22.2 ^{l} of nitrogen weigh 28 ^{g}; hence its formula is N_2.

It is to be carefully noted that a formula represents a definite volume of a substance in the gaseous state. Thus, in the system of elemental weights, the formulas stand for one liter of the gas; in the system of combining weights, for 22.2 ^{l}.

137. What a Formula Means. A formula expresses the following facts in regard to a compound:

1. It shows what elements a compound contains.

2. It specifies what are the weights of each of the component elements in a given volume of a gaseous compound. For example, the formula of ammonia, NH_3, shows that one liter of the gas represented by that formula weighs 0.76 ^{g}, for the sum of the elemental weights of its constituent elements is 0.625 + (3 × 0.045) = 0.76.

3. It indicates the ratio of the weights of the component elements, from which the percentage composition may be calculated. Thus, a liter of water vapor contains 2 × 0.045 ^{g} of hydrogen and 0.715 ^{g} of oxygen, and accordingly weighs 0.805 ^{g}. Knowing this, we can write the proportions:

$$\frac{0.09}{0.805} = \frac{x}{100}$$

$$\frac{0.715}{0.805} = \frac{y}{100}$$

where x and y represent the percentages of hydrogen and oxygen, respectively.   Solving the proportions, we have:

$$x = 11.19$$
$$y = 88.81$$

4. It stands for a definite volume of a gaseous compound.

138. Determination of the Formula of a Compound which can be Vaporized. It is customary to express the results of the analysis of a compound in parts per hundred.   If the percentage composition of a compound and the weight of a liter of it in the gaseous state is known, its formula may be established as illustrated in what follows.

The weight of a liter of water vapor is 0.805 $g.$, and water contains 11.19 per cent of hydrogen and 88.81 per cent of oxygen.

From the proportion:

$$\frac{11.19}{100} = \frac{x}{0.805},$$

$$x = 0.09,$$

it follows that a liter of water vapor must contain 0.09 $g.$ of hydrogen.   But $0.09 = 2 \times 0.045$.   Hence H_2 must occur in the formula.

Likewise from the proportion :

$$\frac{88.81}{100} = \frac{y}{0.805},$$

$$y = 0.715,$$

and 0.715 $g.$ is therefore the weight of the oxygen in one liter of water vapor, and as 0.715 is the elemental weight of oxygen, O must occur in the formula.

The sum of 0.09 and 0.715 is 0.805, and the formula of water vapor must therefore be H_2O.

139. Determination of the Formula of an Involatile Compound. Many compounds are so involatile that the weight of a liter of their vapor cannot be determined. Still formulas may be established for them from their percentage composition, although they are necessarily somewhat ambiguous. Evidently the ratio of the numbers expressing the percentage composition must also be the ratio of the elemental or combining weights, multiplied by the integers 1, 2, 3, 4, and so on, as the case may be.

Suppose, for example, that water could not be vaporized. We know that it contains 11.19 per cent of hydrogen and 88.81 per cent of oxygen. Now the ratio of 11.19 to 0.045 is the same as the ratio of 248.4 to 1 ; and 88.81 : 0.715 :: 124.2 : 1. But the ratio of 248.4 to 124.2 is the same as 2 to 1. Water has therefore the formula, H_2O. It is indeed left undecided as to whether the formula might not also be H_4O_2, H_6O_3, and so on, as the subscripts of these formulas are also in the ratio of 2 : 1. It is customary, however, to choose the simplest ratio.

The same result may be arrived at by the use of combining weights. Thus, in the case of water, the ratio of the percentage of hydrogen to its combining weight is 11.19 : 1, and that of the percentage of oxygen to its combining weight, 88.81 : 16 (or, more accurately, 88.81 : 15.88), which is the same as 5.59 : 1. But 11.19 is twice 5.59; hence the formula is H_2O.

The formula of a compound may thus be found by dividing the percentage of each element by its

elemental or combining weight, and reducing the quotients which denote the number of times a symbol occurs in a formula to the simplest ratio. It may happen that this ratio is not found to consist of whole numbers. Thus, perhaps 1 : 2.03 : 3.98 may have been found. In such cases the slightly differing integral numbers 1 : 2 : 4 may without question be substituted, for the numbers expressing the percentages are obtained by experiment and hence are liable to error. It has ever been found that the more accurate the analysis, the less the numbers in the ratio differ from integers.

140. Formula Weights. The formula weight of a compound is the weight of it in grams numerically equal to the sum of the combining weights of the elements occurring in the formula. The formula weight of nitric acid, HNO_3, is:

$$1 + 14 + (3 \times 16) = 63^{g.}$$

The conception of formula weights leads to a new wording of the Law of the Conservation of Matter:

In any chemical reaction the sum of the formula weights of the factors must equal the sum of the formula weights of the products.

141. Chemical Equations. Chemical equations gain much in simplicity by the use of formulas. The equation representing the burning of hydrogen is:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$
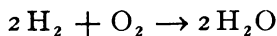
The numerical coefficient denotes that the whole formula is to be multiplied by it just as in algebra. Thus, $2\,H_2O$ means that there are 2×2 hydrogen

symbols and 2×1 oxygen symbols. The combustion of carbon in a limited and in an abundant supply of oxygen is shown thus:

$$2\,C + O_2 \rightarrow 2\,CO$$
$$C + O_2 \rightarrow CO_2$$
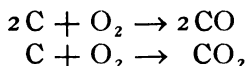
The combustion of (*a*) methane, (*b*) ethylene, and (*c*) acetylene is represented by these equations:

$$\text{(a)} \quad CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$
$$\text{(b)} \quad C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$$
$$\text{(c)} \quad 2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O$$
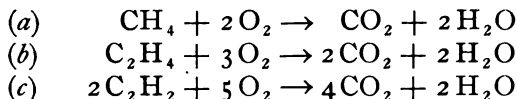
That these equations are in accordance with the Law of the Conservation of Matter is proved by adding the formula weights of the factors and of the products and comparing the two sums for equality. Thus, in the equation for the combustion of acetylene, if we write the formula weights under the formulas and multiply them by the number of times they occur, we have:

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O$$
$$2 \times 26 + 5 \times 32 = 4 \times 44 + 2 \times 18$$
$$52 + 160 = 176 + 36$$
$$212 = 212$$
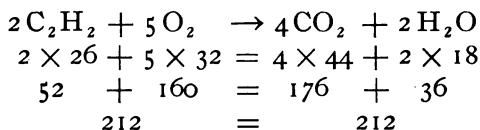
142. Balancing Equations. When the factors and products of a chemical reaction are known and their formulas are written in the form of an equation, it is very seldom that the sums of the formula weights of factors and of products are the same. It is then necessary to increase the number of some or all of the formulas until the formula weights of both factors and products are the same. Among the simplest of chemical reactions are those in

which a substance containing carbon and hydrogen, or carbon, hydrogen, and oxygen is burned; the sole products of such combustions are carbon dioxid and water. We shall accordingly make use of these "combustion equations" in explaining the balancing of equations.

1. To illustrate, suppose we have burned ethylene, C_2H_4, and have found that the sole products are water, H_2O, and carbon dioxid, CO_2. We connect the factors with the plus sign as also the products, and write under the formulas their weights:

$$C_2H_4 + O_2 \rightarrow CO_2 + H_2O$$
$$28 \quad + 32 \qquad 44 \quad + \quad 18$$
$$60 \qquad\qquad 62$$
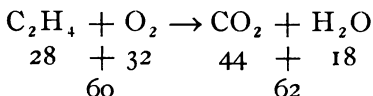
The sums of the formula weights of factors and products are seen to be unequal; the equation is not balanced. As the carbon symbol occurs twice in the factors it must also occur twice in the products, for it stands for a definite weight of carbon. Likewise the hydrogen symbol occurs four times in the factors and but twice in the products. Making the changes thus required, we have:

$$C_2H_4 + O_2 \rightarrow 2\,H_2O + 2\,CO_2$$
$$28 \quad + 32 \qquad 2 \times 18 + 2 \times 44$$
$$60 \qquad\qquad 124$$
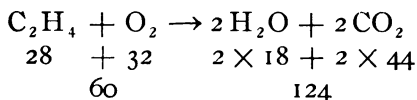
But this makes the oxygen symbol occur six times in the products, while it occurs but twice in the factors. We therefore increase the number of oxygen symbols in the factors to six and then have:

$$C_2H_4 + 3\,O_2 \rightarrow 2\,H_2O + 2\,CO_2$$
$$28 + 3 \times 32 \qquad 36 + 88$$
$$124 \qquad\qquad 124$$
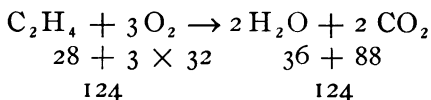
As the sum of the formula weights is now the same on both sides, we write the balanced equation:

$$C_2H_4 + 3O_2 \rightarrow 2H_2O + 2CO_2$$
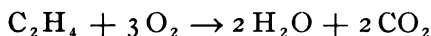
2. As a second example take the combustion of alcohol, C_2H_6O, the products of which are water and carbon dioxid as before. We first write:

$$C_2H_6O + O_2 \rightarrow H_2O + CO_2$$
$$46 + 32 \qquad 18 + 44$$
$$78 \qquad\qquad 62$$
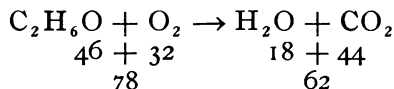
This does not balance, and so we double the number of carbon symbols and treble the number of hydrogen symbols in the products, thus obtaining:

$$C_2H_6O + O_2 \rightarrow 3H_2O + 2CO_2$$
$$46 + 32 \qquad 3 \times 18 + 2 \times 44$$
$$78 \qquad\qquad 142$$
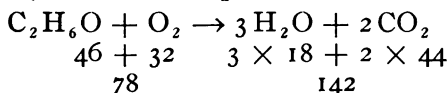
This also does not balance, and we see that while there are seven oxygen symbols in the products, there are but three (one is in the alcohol formula) in the factors. By trebling the oxygen formula, however, we arrive at the balanced equation:

$$C_2H_6O + 3O_2 \times 3H_2O + 2CO_2$$
$$46 + 3 \times 32 \qquad 54 + 88$$
$$142 \qquad\qquad 142$$
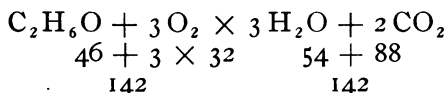
3. Let us consider for a third example the combustion of glycerin, $C_3H_8O_3$, the products of which are, as in the two previous examples, water and carbon dioxid. We first have:

$$C_3H_8O_3 + O_2 \rightarrow 4H_2O + 3CO_2$$
$$92 + 32 \qquad 4 \times 18 + 3 \times 44$$
$$124 \qquad\qquad 204$$
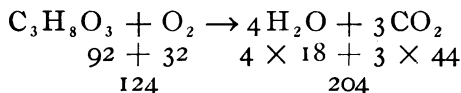
There are now ten oxygen symbols in the products and five in the factors. Subtracting the three

oxygen symbols contained in the glycerin formula, we have seven left. Evidently then we shall have to multiply the O_2 by $7/2 = 3\frac{1}{2}$ in order to balance the equation. But for reasons that will be stated later it is not permissible to use fractional coefficients. To avoid this we multiply the whole equation by two, thus getting the balanced equation:

$$2C_3H_8O_3 + 7O_2 \rightarrow 8H_2O + 6CO_2$$
$$2 \times 92 + 7 \times 32 \quad 8 \times 18 + 6 \times 44$$
$$408 \qquad\qquad 408$$
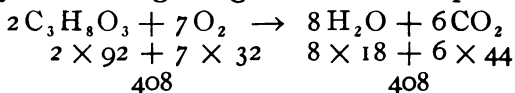
143. The General Procedure. The foregoing illustrations will probably make clear the mechanism of balancing "combustion equations." The formula of the combustible and of oxygen are connected with the plus sign and an arrow is added to show that these factors are converted into the products, carbon dioxid, CO_2, and water, H_2O. The sole products of the combustion of any compound containing carbon and hydrogen, or carbon, hydrogen, and oxygen, are always carbon dioxid and water. Coefficients numerically equal to the subscripts of the carbon and hydrogen symbols in the formula of the combustible are prefixed to the formulas of the carbon dioxid and the water. If, however, the subscript of H in the combustible's formula is an odd number, all the formulas except that of O_2 (which is left to the last) are doubled. When by this procedure the same number of carbon and of hydrogen symbols are obtained in both members, the number of oxygen symbols in the products is counted up, and from this is subtracted the number of oxygen symbols in the formula of the combustible, or the formula doubled, as the case may be. Half of this

difference gives the coefficient of the oxygen formula. If, however, this difference is an odd number, half of it will be a mixed number, and as the coefficients must be integral, all four formulas must be doubled.

These two points should always be borne in mind: (*1*) *The coefficients must be integral.* (*2*) *The sum of the formula weights of the factors must equal that of the products*, or, in other words, *the products must contain the same number of each symbol as the factors.*

144. Volumes. The formula of a gaseous or volatile compound stands for a definite volume of it,— for one liter, when the system of elemental weights is used, and for $22.2^{l.}$ when the system of combining weights is adopted. If the elemental weights of the elements are added together with due allowance for the number of times a symbol occurs in a formula, the weight of a liter of the gaseous compound under standard conditions is obtained. Thus, from the formula of alcohol, C_2H_6O, a liter of alcohol vapor weighs

$$(2 \times 0.536) + (6 \times 0.045) + 0.715 = 2.057^{g.}$$

The equation for the combustion of alcohol (§ 142) may be read:

One liter of alcohol vapor, weighing $2.057^{g.}$, combines with $3^{l.}$ of oxygen, weighing $3 \times 1.43 = 4.29^{g.}$, to give $3^{l.}$ of water vapor, weighing $3 \times 0.805^{g.}$, and $2^{l.}$ of carbon dioxid, weighing $2 \times 1.966^{g.}$.

NOTE. Combustion equations only have thus far been considered. These are not only numerous and important, but are also relatively simple to balance. Later we shall consider the balancing of equations representing reactions other than those of combustion. The general procedure is similar; the same principles hold good.

145. Combustion of Organic Compounds Containing Nitrogen. When any compound containing carbon and nitrogen is burned, the products of the combustion are carbon dioxid and free nitrogen, N_2. If hydrogen is present in the compound, it burns to water. The products of the combustion of compounds containing carbon, hydrogen, oxygen, and nitrogen are then always carbon dioxid, water, and free nitrogen. For example, the balanced equation for the combustion of nitrobenzene, $C_6H_5NO_2$, is:

$$4 C_6H_5NO_2 + 25 O_2 \rightarrow 24 CO_2 + 10 H_2O + 2 N_2$$
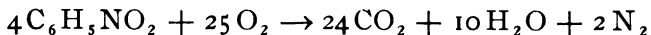
146. Usefulness of Chemical Equations. Equations not only give a simple representation of a chemical reaction, but are also of great value in ascertaining the mass relationships of the reacting substances. Suppose we wish to know how much carbon dioxid and water can be obtained from the total combustion of $50^{g.}$ of turpentine, $C_{10}H_{16}$. The combustion equation is:

$$C_{10}H_{16} + 14 O_2 \rightarrow 10 CO_2 + 8 H_2O$$
$$136 + 448 \qquad 440 + 144$$
$$584 \qquad\qquad 584$$
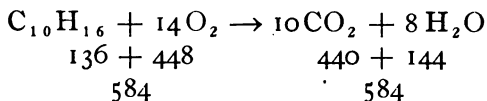
Hence, 136 parts by weight of turpentine combine with 448 parts of oxygen to give 440 parts of carbon dioxid and 144 parts of water. Then $50^{g.}$ of turpentine unites with $50/136 \times 448 = 164.7^{g.}$ of oxygen to yield $50/136 \times 440 = 161.8^{g.}$ of carbon dioxid and $50/136 \times 144 = 52.9^{g.}$ of water. The balanced equation shows what are the relative proportions by weight in terms of the combining weights or formula weights according to which the reaction occurs. As these weights are ratios, it is a

problem of ratio and proportion to convert them into other sets of weights.

ANALYSIS OF ORGANIC COMPOUNDS. Many of the most familiar substances contain carbon united with hydrogen (the hydrocarbons), or with hydrogen and oxygen (alcohols, organic acids, sugars, starch, cellulose, etc.), or with hydrogen, oxygen, and nitrogen (alkaloids, anilin dyes, etc.). It is possible only in extremely few cases to separate the carbon, oxygen, and hydrogen in the free state. Nitrogen, however, is obtained free when compounds containing it are burned. The products of the combustion of these organic compounds are always water, carbon dioxid, and nitrogen, and the method of analyzing them is based upon this fact. A definite weight of the substance is burned in oxygen or is heated with some oxidizing agent, as potassium chlorate or copper oxid, and the products of the combustion passed through tubes containing some deliquescent substance, as calcium chlorid or sulfuric acid, which retains the water, and then through caustic potash solution, which absorbs the carbon dioxid. The nitrogen is collected in a graduated tube over water or mercury.

The increase in the weights of the tubes containing the deliquescent substance and the potash solution gives the weights of the water and the carbon dioxid, respectively, produced by the combustion. As carbon dioxid contains $12/44 = 3/11 = 27.27$ per cent of its weight of carbon, and water $2/18 = 1/9 = 11.19$ per cent of its weight of hydrogen, the weights of the carbon and the hydrogen contained in the compound may easily be found. The sum of the weights of the carbon and the hydrogen thus calculated, subtracted from the weight of the combustible, gives the weight of the other elements present. As we shall consider compounds containing only carbon, hydrogen, oxygen, and nitrogen, and as it has been found best to make a separate determination of nitrogen, the above weight obtained by difference is counted as oxygen.

The results of an analysis are, almost without exception, expressed in per cents. The calculation of the percentage composition is explained in §§ 138 and 139.

Problems

1. If the formula of oxygen is O_2, what do 22.2 *l.* of the gas weigh?

2. If 22.2 *l.* of cyanogen contain 24 *g.* of carbon and 28 *g.* of nitrogen, what is its formula?

3. One liter of hydrazin weighs 1.43 *g.* and contains 0.18 *g.* of hydrogen. What is its formula?

4. Find the percentage composition to two decimals of ammonia, methane, carbon dioxid, alcohol (C_2H_6O), and anilin (C_6H_7N).

5. There is a hydrocarbon called ethane, the weight of 1 *l.* of which is 1.346 *g.* and which contains 80 per cent of carbon. What is its formula?

6. Find the formula of hydrazoic acid, knowing that it contains 97.69 per cent of nitrogen and 2.31 per cent of hydrogen, and that one liter weighs 1.92 *g.*

7. If the elemental weight of sulfur is 1.43 and if 1 *l.* of its gas weighs 2.86 *g.*, what is its formula?

8. Hydrogen dioxid contains 94.12 per cent of oxygen. Calculate its formula.

9. The percentage composition of nitric acid is as follows: $H = 1.59\%$; $O = 76.19\%$; $N = 22.22\%$. Calculate its formula.

10. What are the formula weights of the following substances: Carbon dioxid, water, acetylene, ethylene, methane, alcohol (C_2H_6O), glycerin ($C_3H_8O_3$), acetic acid ($C_2H_4O_2$), benzene (C_6H_6), turpentine ($C_{10}H_{16}$), sugar ($C_{12}H_{22}O_{11}$), camphor ($C_{10}H_{16}O$), starch ($C_6H_{10}O_5$).

11. When any compound of carbon and hydrogen (hydrocarbon), or of carbon, hydrogen, and oxygen, is burned in a plentiful supply of oxygen, the sole products are water and carbon dioxid. Complete and balance the following equations:

(1) $C_2H_4O_2$ $+$ $O_2 \longrightarrow ?$
     (*acetic acid*)

(2) C_6H_6 $+$ $O_2 \longrightarrow ?$
     (*benzene*)

(3) CH_4O $+$ $O_2 \longrightarrow ?$
     (*methyl alcohol*)

(4) C_6H_6O $+$ $O_2 \longrightarrow ?$
     (*carbolic acid*)

(5) $C_{10}H_{16}$ $+$ $O_2 \longrightarrow ?$
     (*turpentine*)
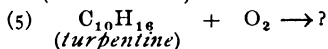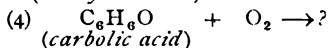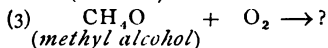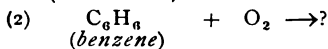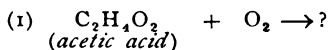
(6) $C_{10}H_{16}O$ $+$ O_2 $\longrightarrow$?
(*camphor*)

(7) $C_{12}H_{22}O_{11}$ $+$ O_2 $\longrightarrow$?
(*sugar*)

(8) $C_6H_{10}O_5$ $+$ O_2 $\longrightarrow$?
(*starch*)

12. Complete and balance, bearing in mind that nitrogen will be separated out in the free state and will have the formula, N_2 :

(1) C_6H_7N $+$ O_2 $\longrightarrow$?
(*anilin*)

(2) C_6H_5N $+$ O_2 $\longrightarrow$?
(*pyridine*)

(3) $C_{17}H_{19}NO_3$ $+$ O_2 $\longrightarrow$?
(*morphine*)

(4) $C_{21}H_{22}N_2O_2$ $+$ O_2 $\longrightarrow$?
(*strychnine*)

(5) $C_{17}H_{21}NO_4$ $+$ O_2 $\longrightarrow$?
(*cocaine*)

13. How many grams of oxygen are required to burn 50 g. of methane, and how many grams of water and carbon dioxid are produced?

Solution : The equation is :

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$$
$$16 \;+\; 64 \qquad 44 \;+\; 36$$
$$80 \qquad\qquad 80$$
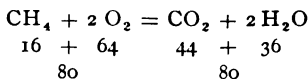
$64/16 \times 50 = 200$, the number of grams of oxygen required.

$44/16 \times 50 = 137.5$, the number of grams of carbon dioxid produced.

$36/16 \times 50 = 112.5$, the number of grams of water produced.

14. 88 g. of carbon dioxid were obtained from the combustion of acetylene. How much acetylene was burned and how much oxygen did it require?

Solution : The equation is :

$$2\,C_2H_2 + 5\,O_2 = 4\,CO_2 + 2\,H_2O$$
$$52 \;+\; 160 \qquad 176 \;+\; 36$$
$$212 \qquad\qquad 212$$
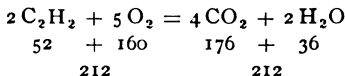
$52/176 \times 88 = 26$, the number of grams of acetylene.

$160/176 \times 88 = 80$, the number of grams of oxygen.

15. How much oxygen does it take to just burn 156 g. of benzene, C_6H_6, and how much water and carbon dioxid are produced?

16.   22 g. of carbon dioxid were obtained by the burning of alcohol, C_2H_6O. How much alcohol and oxygen were required?

17.   How much starch, $C_6H_{10}O_5$, has to be burned to give 72 g. of water?

18.   How many grams of nitrogen and of water are obtained from the combustion of 100 g. of anilin, C_6H_7N?

19.   Turpentine is a hydrocarbon. 0.880 g. of CO_2 and 0.288 g. of H_2O were obtained when 0.272 g. of it were burned. What is its percentage composition?

Solution: 0.880 g. of carbon dioxid contains 0.880 × 12 / 44 = 0.240 g. of carbon, and 0.288 g. of water contains 0.288 × 1 / 9 = 0.032 g. of hydrogen. Then 0.272 : 0.240 : : 100 : x, whence $x =$ 88.24, the percentage of carbon; and 0.272 : 0.032 : : 100 : y, whence $y =$ 11.76, the percentage of hydrogen.

20.   Camphor contains carbon, hydrogen, and oxygen. 0.608 g. were burned and yielded 1.760 g. of CO_2 and 0.576 g. of H_2O. Find its percentage composition.

21.   0.4536 g. of starch (which contains carbon, hydrogen, and oxygen) yielded when burned 0.7392 g. of CO_2 and 0.2521 g. of H_2O. What is its percentage composition?

22.   If a liter of turpentine vapor weighs 6.08 g., find its formula from the percentage composition calculated in Problem 19.

23.   Find the formula of camphor, knowing its percentage composition (Problem 20) and that 22.2 l. of its vapor weigh 152 g.

24.   What is the simplest formula for a compound containing 72.44 per cent of carbon, 6 09 per cent of hydrogen, and 21.47 per cent of oxygen?

25.   What is the volume at 20° and 746^{mm}. of the nitrogen given off in the combustion of 16.84 g. of a compound whose formula is $C_6H_5O_2N_3$?

THE ATOMIC THEORY—VALENCE

147. The Constitution of Matter. Two hypotheses as to the constitution of matter merit attention here:

1. Matter may be perfectly continuous in structure, a vacuum or empty portion of space being regarded as impossible.

2. Matter may consist of separate and distinct parts more or less isolated in space.

Opinions differ as to which of these two hypotheses represents the facts the better, but inasmuch as the second gives a simple explanation of the Laws of Chemical Combination, it has become interwoven with the chemistry of the nineteenth century; so much so, indeed, that the theory is often considered by some as of more importance than the facts which it is supposed to account for. But it should ever be kept in mind that a hypothesis or theory is necessarily temporary and is subordinate to the facts.

148. Atoms and Molecules; Electrons. Matter then is supposed to consist of a multitude of minute particles of definite mass more or less separated in space. Suppose a piece of paper to be torn up into as small bits as possible, and let these bits be cut up into as many parts as the finest razors will permit; the paper still remains paper. Let us imagine the division to be carried further and further. We

shall arrive finally at such a small piece of paper that it cannot be divided again without its ceasing to be paper. We then say that we have to do with a *molecule* of paper.

Generally speaking, a molecule may be defined as *the smallest part of matter that can exist in a free state and retain the properties of the substance.*

But the molecule of paper can be divided further into still smaller parts, which have been given the name of *atoms*. The atoms in this case are, however, not paper, but the elements composing paper, namely, carbon, hydrogen, and oxygen.

Until recently it has been supposed that *atoms are the smallest parts into which elements can be divided.* But it is now known that there exist still smaller particles which are called *electrons*. Their existence has been brought to light by electrical means, and does not affect essentially the views on atoms which chemists have held.

A few elements, as mercury and some other metals, seem to have their atoms and molecules identical; but, as a rule, atoms of the same kind unite to form molecules. Thus, the molecules of the elementary gases we have studied consist of two atoms each. This is in accordance with the fact that the weight of a liter of any of these gaseous elements is double its elemental weight. As we shall see later, the elemental and combining weights are proportional to the weights of the atoms themselves.

There are as many different kinds of atoms as there are of elements, but the number of different kinds of molecules is boundless. It has been calculated that, if a single drop of water were magnified

to the size of the earth, the molecules would be a little larger than base-balls. This may give some idea of the minuteness of atoms and molecules and of the enormous number of them contained in even the smallest portion of matter we are able to perceive with the aid of our most powerful microscopes.

HISTORICAL NOTE. The conception of matter as being made up of atoms endowed with certain properties or qualities is quite ancient. It was first propounded by the Greek philosophers, Leucippus and Democritus, in the fifth century, B. C. Their conception of atoms was a mere speculation, however, and it was not until the beginning of the nineteenth century that it was revived by John Dalton to account for the Laws of Definite and Multiple Proportions.

149. The Atomic Theory. The usefulness of the hypothesis of atoms lies in the simple account it renders of the Laws of Definite and Multiple Proportions, and the hypothesis has consequently been elaborated into a theory. We have learned that when elements combine with one another the union takes place according to fixed proportions, and that the analysis of any sample of a definite chemical compound always gives the same results. Now we are quite free in our choice of units to express the combining proportions of the elements; we may use grams, tons, pounds, or any other unit of mass we see fit. We have already employed two ways of expressing the ratio of the quantities of elements in compounds. In one we took the smallest weight in grams contained in a liter of any of their gaseous compounds, and called these weights the elemental weights. In the other we chose the parts by weight that express the ratios when referred to hydrogen

as unity, and called these weights the combining weights. But we might also adopt numbers meant to represent the weights of the atoms themselves. If the mass of a hydrogen atom be taken as unity, the masses of the carbon, nitrogen, and oxygen atoms are 12, 14, and 16 times the unit mass, respectively. Our ignorance of the actual weights of the atoms is no hindrance, for these sets of numbers are ratios and hence independent of the unit we adopt.

The relationships which have been established for the combining weights can then be expressed in terms of atomic weights. The molecular weights of the elements will depend upon the number of atoms which compose their molecules. In the case of hydrogen, nitrogen, and oxygen the molecular weights are double the atomic weights. As we do not know how many atoms compose the carbon molecule, we are forced to assume that its molecular and atomic weights are the same. The molecular weight of a compound is equal to the sum of the atomic weights of the elements composing it. Thus, the molecular weight of water is 18; that of carbon dioxid, 44.

150. Laws Accounted for by This Theory. If then we assume that on an average the atoms of the same element have equal masses, we can readily account for the Laws of Definite and Multiple Proportions. Thus, one or more atoms of one element may combine with one or more atoms of another element to form a molecule of a compound containing both elements. For example, one atom of carbon combines with one atom of oxygen to produce one molecule of carbon monoxid, CO. Also, one atom of carbon combines with two atoms of

oxygen to form one molecule of carbon dioxid,
CO_2. Now, since atoms are indivisible, one carbon
atom cannot combine with, say, one and a half or one
and a fifth, of an oxygen atom, for fractional atoms
are supposed not to exist. Combination must take
place between whole atoms, and when several com-
pounds may be prepared from two or more atoms
of different elements, only integers can represent
the numbers of atoms. The Laws of Definite and
Multiple Proportions follow necessarily. Fractions
of atoms cannot exist; hence combinations between
atoms must be expressible by integers.

The atomic theory supposes then that what we
observe in any chemical action is the result of a
vast number of similar actions occurring between
the atoms.

The atomic theory will be applied from now on.
Instead of speaking of elemental or combining
weights, we shall say atomic and molecular weights.
The symbols and formulas shall stand for the vol-
umes and weights of atoms and molecules. Thus,
the formula for alcohol, C_2H_6O, stands for the vol-
ume which the alcohol molecule in the gaseous
state occupies, and shows that the molecule consists
of two atoms of carbon, six of hydrogen, and one of
oxygen. It has been more or less roughly esti-
mated that a liter of any elementary gas contains
about 1,000,000,000,000,000,000,000,000 molecules, so
that the weight of one molecule of hydrogen is
$\frac{0.09}{10^{24}}$ grams, an extremely small number. It is of
no particular advantage, however, to know the exact
weight of an atom or a molecule.

VALENCY

151. Equations in Terms of Molecules and Atoms. Let us again consider the combustion of alcohol. We know that its formula in the gaseous state is C_2H_6O, so that in terms of the Atomic Theory a molecule of alcohol is made up of two atoms of carbon, six of hydrogen, and one of oxygen. We also know how many atoms are contained in a molecule of oxygen, O_2, and in a molecule of water, H_2O, and carbon dioxid, CO_2. Now atoms are indestructible; hence the number of atoms in the factors of a reaction must equal the number of atoms in the products. In order to balance an equation we accordingly proceed as set forth on page 131, bearing in mind that if the same number of atoms of a kind are in both members of the equation, it is balanced. The sum of the molecular or atomic weights of the factors of a chemical reaction is then equal to the sum of the molecular or atomic weights of the products.

152. Value of Chemical Equations. Equations do not tell everything about a reaction; they are usually but ideal or rather perhaps average expressions of the facts. Variations in temperature, pressure, and strength of reagents cause considerable variations in reactions. A reaction taking place according to one equation under certain conditions may proceed according to quite a different equation when the conditions are changed. Equations tell the quantitative facts under special qualitative conditions, and attempt nothing more. They are of value, however, but should be used with proper limitations.

153. Valency. We have seen that one volume of oxygen combines with two volumes of hydrogen to produce two volumes of water vapor; that one volume of nitrogen combines with three volumes of hydrogen to produce two volumes of ammonia, and later we shall learn that one volume of chlorin combines with one volume of hydrogen to yield two volumes of hydrogen chlorid. From these instances it is apparent that different elements have different capacities for combination, and we shall find that this is generally true. This power of combination is characteristic of an element, and is called its *valency*.

A consideration of the following formulas may serve to illustrate valency:

$$HCl \qquad H_2O \qquad H_3N \qquad H_4C$$

It is seen that carbon, for instance, unites with four times as much hydrogen as does chlorin.

Hydrogen is assumed to have unit valency; it is *univalent*. Then chlorin is univalent also, for one volume of chlorin combines with one volume of hydrogen. As two volumes of hydrogen unite with one volume of oxygen, the valency of oxygen is twice that of hydrogen; it is *bivalent*. Likewise, the valency of nitrogen and of carbon is *triple* and *quadruple* that of hydrogen, respectively, and these two elements are therefore *trivalent* and *quadrivalent*. But few elements exhibit a valency of more than four.

Radicals also have a valence. Ammonium (NH_4) and hydroxyl (OH) are univalent, while (SO_4) is bivalent.
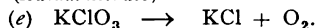
154. Variable Valency. The combining power or valency of an element is not always the same. Oxygen in water is bivalent, but in hydrogen dioxid, H_2O_2, it appears univalent. Also, carbon, which is quadrivalent in methane, CH_4, and in carbon dioxid, CO_2, seems bivalent in carbon monoxid, CO. Many other instances of variable valency will be encountered later. Elements exhibit at times one valency toward certain elements and another toward other elements. Valence is probably a mutual property of elements and depends upon the conditions according to which a compound is formed.

Problems

1. The valency of the following elements is indicated by the number of accents: Na′ (sodium), K′ (potassium), Ca″ (calcium), Al‴ (aluminum). What are the formulas of the chlorids and the oxids of each of the elements, if chlorin (Cl) is univalent and oxygen bivalent?

2. If one liter of bromin vapor weighs 7.2 g., and if one gram of hydrogen combines with 80 g. of bromin, what is the valency of bromin?

3. Balance the following equations. In equations (*a*) to (*c*) a large proportion of water is supposed to be present but not participating in the reaction.

(*a*) Zn   +   HCl $\longrightarrow$ $ZnCl_2$ + H_2.
   (*zinc*)   (*hydrochloric acid*)   (*zinc chlorid*)

(*b*) Zn   + H_2SO_4 $\longrightarrow$ $ZnSO_4$ + ?
           (*sulfuric acid*)   (*zinc sulfate*)

(*c*) NaCl   + H_2SO_4 $\longrightarrow$ Na_2SO_4 + HCl.
(*sodium chlorid*)   (*sodium sulfate*)

(*d*) $NaNO_3$ + H_2SO_4 $\longrightarrow$ Na_2SO_4 + HNO_3.
(*sodium nitrate*)

(*e*) $KClO_3$ $\longrightarrow$ KCl + O_2.

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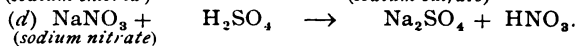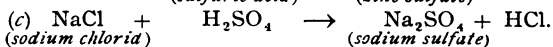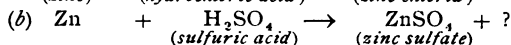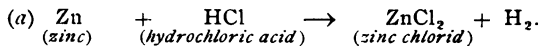
CHAPTER XIV

SALTS, ACIDS, AND BASES

Salts, acids, and bases are so common and valuable, and their reactions and properties are of such importance, that they demand attention even before some of the elements entering into their composition.

155. Early Meaning of the Terms Salt, Acid, Alkali, and Base. Originally the word "salt" was applied to common table salt alone, but as in the course of time other substances were found which resembled table salt in certain particulars, such as color, taste, and solubility, the same name was given to them also, often with the qualification of some proper noun, as Epsom salt, Rochelle salt, Glauber's salt.

The word "acid" signifies *sour*, and was given to such substances as possess a sour taste. Vinegar and lemon juice were among the first acids known.

The word "alkali" originally meant *ashes*, and was the name given to the soluble constituents of wood ashes, which had a bitter, brackish taste and a soapy feel. It was later found that acids and alkalis possessed opposite properties in several respects. Thus, litmus, a dyestuff extracted from certain lichens, is turned red when moistened with an acid liquor, and blue with an alkalin, and can be made to change color any number of times by immersion in first one and then the other of the

two liquors. Other vegetable extracts also undergo similar changes of color. It was also found that when an acid solution was mixed with an alkalin one, for certain proportions of the two liquids their mixture did not affect the color of litmus, and instead of tasting sour or bitter, tasted salty. The acid and alkali *neutralized* each other's properties, and a new substance was formed which had the general properties of the class of substances known as salts. As other substances were found to behave like alkalis in many respects, without being so bitter and corrosive, the name of alkali was gradually restricted to a few substances only, the most important of which are caustic soda (sodium hydroxid) and caustic potash (potassium hydroxid). The name of "base" was then assigned to the whole class of substances acting like alkalis toward acids, *i. e.*, combining with them to form salts.

After the discovery of oxygen and hydrogen and of the composition of water, and as methods of chemical analysis were improved, it was found that all acids contained hydrogen, and all bases both hydrogen and oxygen, combined in the radical, hydroxyl, OH. Furthermore, salts were found to be composed of two parts, one of a metallic, the other of a non-metallic nature.

156. Acid Defined. An *acid* is a compound which has usually a sour taste, changes the color of many substances, as litmus, to red, and reacts with a base to produce a salt and water. It is composed of a non-metallic element or radical and hydrogen ; the hydrogen can be replaced by a metal to form a salt.

157. Base Defined. A *base* is a compound which restores the color of dyestuffs that has been changed by an acid, and reacts with an acid to produce a salt and water; it is composed of a metal or metal-like radical and the radical, hydroxyl, OH.

158. Alkali Defined. An *alkali* is a strong, caustic base, very soluble in water. Potassium hydroxid, KOH, sodium hydroxid, NaOH, and ammonium hydroxid, $(NH_4)OH$, are the three common alkalis. The first two are sometimes called the *fixed alkalis* in contradistinction to the last, which is called the *volatile alkali,* as heat readily vaporizes it.

159. Salt Defined. A *salt* is a compound usually without action on vegetable dyes. It may be prepared by neutralizing solutions of an acid and a base, as well as in other ways (Chapter XVI.). It is composed of a metal or metal-like radical and a non-metal or non-metallic radical.

THE THEORY OF ELECTROLYTIC DISSOCIATION. The foregoing definitions represent fairly well the state of our knowledge of the nature of acids, bases, and salts up to the year 1887, when Arrhenius, a Swedish chemist, brought to light the importance of a certain property of salts, acids, and bases, and ventured a hypothesis with reference to it, which has been elaborated into a most fruitful theory. This property is that of electric conductance. Hittorf, indeed, in 1840, had shown that all solutions that conduct electricity are solutions of salts, acids, or bases, but this attracted little attention at that time. Arrhenius, however, brought it into close connection with a number of other properties of solutions of which it offers a simple explanation. It also gives a simple account of electric conductance in solutions.

ELECTRIC CONDUCTANCE. It is obvious that a fluid may be transferred from one place to another in two essentially different ways; it may flow over through

pipes or it may be carried over in buckets. Analogously, electricity may be transferred from one place to another in two ways. The flow of electricity through or along a metallic wire (conductor of the first class) corresponds to the first way, while its flow through a solution (conductor of the second class) corresponds to the second way. The carriers of the electricity in conductors of the second class are the two parts of the salt, acid, or base, or the *ions*, as they are named.

When the ends, the *electrodes*, of an electrical circuit are at a different electrical level or potential and are immersed in any solution of an acid, base, or salt, the metallic (hydrogen) ions or *cations* carry the positive electricity towards one end of the circuit, the *cathode*, while the non-metallic (hydroxyl) ions or *anions* carry the negative electricity towards the other end of the circuit, the *anode*. Both anions and cations carry equal and definite amounts of negative and positive electricity, respectively. This phenomenon is known as *electrolysis*, and the solution is called an *electrolyte*.

It is natural to inquire how these carriers of electricity, these ions, come into existence when a salt, acid, or base is dissolved, for these compounds when perfectly dry do not conduct electricity at all. It was formerly supposed that they were formed by the action of the electric current, but Arrhenius proposed another explanation, sometimes called the Ionization Theory.

THE IONIZATION THEORY. Arrhenius assumed that when a salt, acid, or base dissolves, the very act of solution breaks it up more or less into its ions. The solvent seems to act much as a change of temperature or pressure does in effecting the dissociation of a compound. (Cf. page 60.) Just as a rise of temperature or diminution of pressure causes a greater and greater degree of dissociation of many substances, so does an augmentation of the proportion of the solvent in a solution increase the degree of dissociation of the dissolved substance ; for infinite dilutions the dissociation is complete, just as is the case in ordinary dissociation with infinitely high temperatures or low pressures.

To distinguish the dissociation of a salt, acid, or base by a solvent from ordinary dissociation, the former is

termed *electrolytic dissociation,* and Arrhenius' Ioni-
zation Theory is often called the Theory of Electrolytic
Dissociation.

How a Solution Conducts Electricity. Suppose
a salt, whose metallic part we shall denote by M, and
non-metallic part by A, to be dissolved in water.   To
simplify matters we shall assume M and A both to be
univalent, and that the proportion of water is so great
that the salt MA is practically totally dissociated into
its icns.   This dissociation may be represented by the
following equation :

$$MA \rightarrow \overset{+}{M} + \overset{-}{A}$$
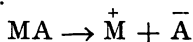
where the superposed signs + and — mean that the
respective ions are charged with positive and negative
electricity.   Inasmuch as there are present in the solu-
tion the same number of cations and anions charged
with equal quantities of electricity—the cations with
positive, the anions with negative—the solution as a
whole is electrically neutral.   If now two electrodes be
placed in the solution and a current of electricity passed
through it, the cations will be attracted by and move
towards the negative electrode, and the anions will be
attracted by and move towards the positive electrode.
There will thus be two processions of ions moving in
opposite directions.   The speed with which they move
depends mainly upon their nature, the temperature, and
the viscosity of the solution.

The ions on arriving at the electrodes give up their
electrical charges and become changed into electrically
neutral atoms or molecules, which may react with the
solvent to form other compounds or may escape from it.

The foregoing is an outline of what is supposed to
occur in the electrolysis of any soluble salt.   If there
should be any doubt in the case of a certain substance
as to what the two parts of a salt are, its electrolysis and
subsequent examination of the electrodes or of the
solution in the vicinity of the electrodes will clear up
the doubt.   .

Acids, Bases, and Salts Defined in Terms of Ions.
Solutions of acids, bases, and salts alone are electrolytes.
The term salt includes bases and acids.   In addition to

the properties already given as characteristic of these classes of compounds, the following statements may be made :

Salts are compounds of an anion and a cation.

Acids are salts whose cation is always hydrogen, not free gaseous hydrogen, but ionic hydrogen. The general properties of acids are those of the hydrogen ion. Thus, the sour taste and the reddening of litmus are done by the hydrogen ion, no matter what the anion it may be combined with to form the acid.

Bases are salts whose anion is always hydroxyl. The general properties of bases are those of the ion, hydroxyl.

SALTS, ACIDS, AND BASES COMPARED IN THE LIGHT OF THE IONIZATION THEORY. Salts, acids, and bases have the same general structure ; they consist of an electro-positive element or radical (cation) combined with an electro-negative element or radical (anion), only acids always have hydrogen for cation and bases always hydroxyl for anion. Acids are hydrogen salts ; bases are hydroxyl salts. All three classes undergo electrolytic dissociation when dissolved in water, and their solutions conduct electricity. Acids and bases unite to produce salts, while their hydrogen and hydroxyl ions combine to form water. Thus, if HA and C(OH) represent an acid and base, respectively, their reaction is illustrated by the equation :

$$(\overset{+}{H} + \overset{-}{A}) + (\overset{+}{C} + \overline{HO}) \rightarrow (\overset{+}{C} + \overset{-}{A}) + H_2O$$
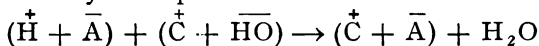
160. Acid, Alkalin, and Neutral Reactions. A solution is said to have an acid reaction when it tastes sour and changes the color of such substances as blue litmus and other vegetable colors. It is said to have an alkalin reaction when it tastes bitter and restores the color of the substances changed by acids. A solution is neutral when it tastes neither sour nor alkalin and has no effect on litmus. Acid reactions are due to the presence of hydrogen ions; alkalin reactions to the presence of hydroxyl ions.

161. Indicators. Indicators are substances which have different colors in acid and alkalin solutions. The requisites of a good indicator are that a small proportion of it will tinge a large amount of solution and will change its color promptly and decidedly when the solution changes from an acid to an alkalin reaction, and *vice versa*. Litmus is the time-honored indicator, but many others are known, as Congo red, phenolphthalein, and methyl orange.

162. Nomenclature of Acids, Bases, and Salts. Bases are called *hydroxids* of metals, as sodium hydroxid, NaOH, and calcium hydroxid, Ca(OH)$_2$. The names of acids not containing oxygen (*hydracids*) are distinguished by the termination "ic" and the prefix "hydro," as hydrochlor*ic* acid. The names of the commonest acids containing oxygen (*oxacids*) also terminate in "ic," as sulfur*ic* acid, H$_2$SO$_4$. Acids containing less oxygen have names ending in "ous," as sulfur*ous* acid, H$_2$SO$_3$, and with less oxygen still, the prefix "hypo" is added, as *hypo*chlorous acid, HClO. Acids containing more oxygen than do the commoner ones have names beginning with "per," as *per*chloric acid, HClO$_4$.

Salts formed from hydracids have names ending in "id," as sodium chlorid, NaCl. The nomenclature of the salts of the oxacids is patterned after that of the acids, thus:

"ic" acids yield "ate" salts, as calcium sulf*ate*, CaSO$_4$.

"ous" acids yield "ite" salts, as calcium sulf*ite*, CaSO$_3$.

The prefixes "hypo" and "per" are retained, as

potassium *hypo*nitrite, KNO, and potassium *per*chlorate, $KClO_4$.

Ions. Much of chemistry consists in the study of acids, bases, and salts, especially when dissolved in water. But these compounds break up more or less into their ions when dissolved in water, and the ions are in a measure independent of one another. Hence it is not really the reactions of the acids, bases, and salts in the pure state, that is, free from water, that we study, but rather the reactions of their ions. It is necessary then that we have a clear idea of what an ion is.

THE HYDROGEN ION. Ions, as such, exist only in solution. A molecule of gaseous hydrogen is a very different thing from an ion of hydrogen. With the properties of the hydrogen molecule we have already become acquainted (Chapter IV.). Some of the properties of hydrogen ions are these : (*1*) They can exist only in solution, and then only when an equivalent number of ions of some non-metallic element or radical is present ; (*2*) they are charged with enormous quantities of positive electricity, and can become molecules of hydrogen only when this electrical charge is neutralized by an equal amount of negative electricity ; (*3*) they move about at random in the solution, but when a current of electricity is sent through it, they move with a speed depending upon the temperature and the nature of the solvent toward the negative pole, where their positive charge is neutralized with an equal negative charge, and gaseous hydrogen is formed. Analogous properties are characteristic of every ion.

THE IONS OF THE ELEMENTS THUS FAR STUDIED. The hydrogen ion is that which characterizes an acid as such, and has been described above. Oxygen does not form simple ions, but the hydroxyl ion is the anion of all bases. Nitrogen does not assume the ionic condition by itself, except perhaps in hydrazoic acid, HN_3. The ammonium radical (NH_4) forms a cation similar in many respects to those of potassium and sodium. Carbon also does not assume the ionic condition, although the radical, cyanogen, CN, is the anion of hydrocyanic acid, HCN.

REACTIONS OF IONS. The reactions between bases, acids, and salts in aqueous solution are almost entirely reactions between their ions. Thus, a solution of sodium chlorid, NaCl, consists largely of the ions $\overset{+}{Na}$ and $\overset{-}{Cl}$. Likewise, a solution of silver nitrate, $AgNO_3$, contains a large number of $\overset{+}{Ag}$ and $\overset{-}{NO_3}$ ions. When these solutions are mixed, silver chlorid, AgCl, which, being insoluble, does not break up into ions, and sodium nitrate, $NaNO_3$, consisting of the ions, $\overset{+}{Na}$ and $\overset{-}{NO_3}$, are produced. The reaction may be represented thus:

$$(\overset{+}{Ag} + \overset{-}{NO_3}) + (\overset{+}{Na} + \overset{-}{Cl}) \rightarrow AgCl + (\overset{+}{Na} + \overset{-}{NO_3})$$
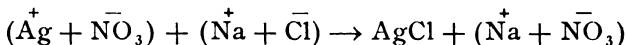
If, however, sodium chlorate, $NaClO_3$, which consists mainly of the ions $\overset{+}{Na}$ and $\overset{-}{ClO_3}$, be added to a solution of silver nitrate, the silver chlorate which might be formed is not precipitated, since it is soluble in water. The chlorin in sodium or silver chlorate is not an ion itself, but is a part of the chlorate ion, $\overset{-}{ClO_3}$. There is no apparent result then when the solutions of silver nitrate and sodium chlorate are mixed, and the solution behaves as if all four possible combinations of the ions $\overset{+}{Ag}$, $\overset{+}{Na}$, $\overset{-}{NO_3}$, and $\overset{-}{ClO_3}$ were present. Many other reactions might be given in which compounds containing the same element react differently because in one of the compounds the element is in one ionic condition, while in others it is in another.

NOTE. Most of the substances thus far studied are gases or insoluble solids, and hence there has been but little need of the Ionization Theory. The majority of substances which remain to be studied, however, are salts, acids, or bases, and to be consistent, perhaps, the theory should be applied in a thoroughgoing manner. This will not be done, however, mainly because the theory cannot be said to be on a perfectly sure foundation, and also because it is not accepted by all chemists of note. It is an interesting and profitable exercise, nevertheless, to interpret reactions in terms of ions.

CHAPTER XV

NITROGEN OXIDS AND OXACIDS

163. Nature of Combination. Nitrogen combines with oxygen slowly when electric sparks are passed through a mixture of the two gases (Fig. 9). The combination takes place with absorption of heat and ceases as soon as the passing of the sparks is stopped. The reason for this behavior is that the kindling point of nitrogen, *i. e.*, the temperature at which nitrogen starts to burn, is far above the temperature produced by the combustion. This behavior is the direct opposite of that observed in the union of hydrogen and oxygen (page 44), where the combination is accompanied with an evolution of heat, and the electric spark serves only to start the reaction in a small portion of the mixture, which then spreads rapidly throughout it.

In all, there are five oxids of nitrogen, which offer an excellent illustration of the Law of Multiple Proportions, but seem contrary to the rules of Valence. The oxids of nitrogen do not occur free in nature except, perhaps, in small amounts during thunder storms, when a union of the two elements is brought about by lightning flashes. The ammonia which may also be formed during the storm generally combines with the oxids. The method commonly used in their preparation consists in decomposing nitric acid or nitrates by the action of heat alone or aided by some metal or acid.
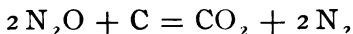
NITROUS OXID, N₂O

164. Preparation. When ammonium nitrate, a compound of ammonia and nitric acid, is heated to about 200°, it decomposes into nitrous oxid and water:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

If the temperature is above 300°, nitric oxid is also formed in small amounts.

165. Properties. *Physical.* Nitrous oxid is a colorless gas of a sweetish taste and a pleasant odor. It is soluble in somewhat less than its own volume of water.

Chemical. Nitrous oxid supports the combustion of wood, phosphorus, and most other substances quite as well as does oxygen, but as the substances have a higher kindling temperature in it than in oxygen, they need to be well ignited before being introduced into the gas. The equation for the combustion of carbon in this gas is:

$$2N_2O + C = CO_2 + 2N_2$$

Physiological. When mixed with about a quarter of its volume of oxygen (air) and inhaled, nitrous oxid produces a peculiar intoxication and excites laughter; hence the popular name of "laughing gas." When inhaled in the pure state, it produces intoxication, then insensibility, and ultimately death. It supports respiration longer than any other gas except oxygen.
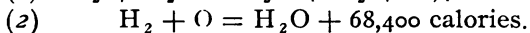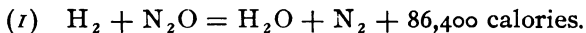
COMPOSITION. Equal volumes of nitrous oxid and of hydrogen are mixed and exploded in an eudiometer. There results a contraction of one-half, and the residual gas is found to be nitrogen. The contraction

represents the volume of water vapor formed, and as one volume of water vapor consists of one volume of hydrogen and one-half volume of oxygen, one volume of nitrous oxid contains one volume of nitrogen and one-half volume of oxygen. As the weight of one liter of this gas is 1.965 $g.$ it follows that its formula is N_2O, for 1,965 = 2 × 0.625 (the elemental weight of nitrogen) + 0.715 (the elemental weight of oxygen).

166. Uses. Nitrous oxid is used by dentists to produce insensibility during the extraction of teeth. For that purpose it is liquefied and stored in strong cylinders provided with stopcocks.

HEAT OF FORMATION OF NITROUS OXID. Both hydrogen and carbon burn much more vigorously in nitrous oxid than they do in oxygen, and consequently the liberation of heat must be greater. This indicates that the heat of formation of this oxid of nitrogen is negative; it is an endothermic compound. Its heat of formation has then to be determined indirectly. How this is done is illustrated by the following thermochemical equations, in which the formula weights of the substances are used:
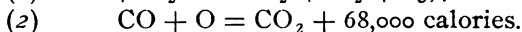
FIRST METHOD

(*1*) $H_2 + N_2O = H_2O + N_2 + 86,400$ calories.
(*2*) $H_2 + O = H_2O + 68,400$ calories.

By subtraction of (2) from (1) and transposition.

(*3*) $N_2 + O = N_2O - 18,000$ calories.

SECOND METHOD

(*1*) $CO + N_2O = CO_2 + N_2 + 85,400$ calories.
(*2*) $CO + O = CO_2 + 68,000$ calories.

By subtraction of (2) from (1) and transposition,

(*3*) $N_2 + O = N_2O - 17,400$ calories.
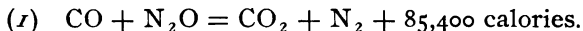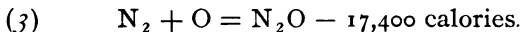
Both of these calculations are based on experimental results, which are of course subject to error. Taking their average, we have 17,700 calories as the heat absorbed in the formation of 44 $g.$ of nitrous oxid.

NITRIC OXID, NO

167. Preparation. When dilute nitric acid is brought in contact with many metals, especially copper, mercury, or silver, reaction takes place readily, and nitric oxid is the main gaseous product. It may also be obtained by the action of nitric acid on ferrous sulfate (green vitriol).

168. Properties. *Physical.* Nitric oxid is a colorless gas, the taste and odor of which cannot be ascertained, as it combines with oxygen on coming in contact with the air, forming the tetroxid.

Chemical. While but slightly soluble in water, nitric oxid is very soluble in a solution of ferrous sulfate, with which it forms a brown compound of the two substances. As nitric oxid decomposes at temperatures above 600°, some substances may be made to burn in it, provided their heat of combustion is sufficient to decompose the oxid of nitrogen. Thus, phosphorus, if ignited and introduced into the gas, will continue to burn, while sulfur and charcoal will not. Nitric oxid combines readily with oxygen to form nitrogen dioxid, a deep brown gas quite soluble in water.

NOTE. Priestley in 1772 observed that when one volume of nitric oxid was mixed with two volumes of air in a tube over water there was a diminution of one-fifth of a volume. This observation was made before the discovery of oxygen; hence he could not draw the conclusion that we can to-day, *viz.*, that one-fifth of the volume of the air is oxygen.

COMPOSITION. One volume of nitric oxid, when heated with sodium or finely divided iron or copper, undergoes a diminution of one-half. The residual gas is nitrogen; the oxygen has combined with the metal. Nitric oxid therefore contains equal volumes of nitrogen

and oxygen.   One liter weighs 1.34 $^{g.}$, which is equal to the sum of 0.625 (the elemental weight of nitrogen) and 0.715 (the elemental weight of oxygen).

169. Uses. The property that nitric oxid has of combining directly with oxygen plays a fundamental role in the manufacture of sulfuric acid; great quantities of it are used in that process.

170. Nitrogen Trioxid, N_2O_3. Nitrogen trioxid is obtained as a blue liquid when nitric oxid is passed into liquefied nitrogen tetroxid, N_2O_4, at temperatures below –21°.   It decomposes at higher temperatures into a mixture of nitrous and nitric oxids.

171. Nitrogen Pentoxid. Nitrogen pentoxid is prepared by the action of phosphorus pentoxid on very concentrated nitric acid at low temperatures. It is a white, crystalline substance melting at 30° with partial decomposition, while at 47° it decomposes rapidly into oxygen and nitrogen dioxid.

172. Nitrogen Dioxid and Tetroxid (Peroxid). Nitrogen dioxid and tetroxid may be prepared (*1*) by mixing two volumes of nitric oxid with one of oxygen, and (*2*) by heating lead or manganous nitrate.

At low temperatures nitrogen peroxid is a colorless solid, melting at –12° into a light yellow liquid which, as the temperature rises, assumes a deeper and deeper tint.   At 25° the liquid boils, giving off a vapor of a reddish-brown color.   The color of this vapor deepens as the temperature continues to rise, until at 50° it is so brown as to be almost opaque.   When the temperature is lowered, the reverse changes occur; we have to do with a reversible reaction.

NITRIC ACID

173. Occurrence. Free nitric acid is not met with in nature except in minute amounts in the air after thunder storms.   It usually combines with the ammonia which has also been formed by the action
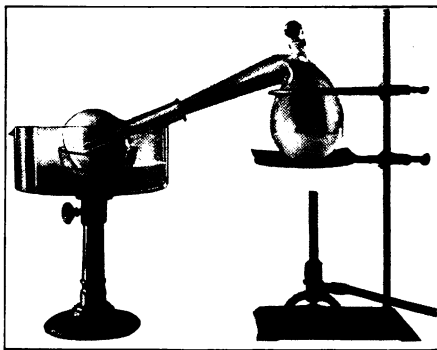

Fig. 32 — A CONVENIENT ARRANGEMENT OF APPA-
RATUS FOR PREPARING NITRIC ACID

of the lightning flashes, and the resulting compound, ammonium nitrate, is washed down in the soil.   Compounds of nitric acid with the metals sodium and potassium are found in large beds in certain places, and are known as *niters* or *saltpeters.* These compounds are formed by the action of a microörganism upon substances of animal and vegetable origin containing compounds of nitrogen as well as of potassium and sodium.

HISTORICAL NOTE.   The old chemists called nitric acid "spirits of niter" because it was formed as vapor ("spirit") when niter was heated with alum, which contains sulfuric acid in combination.   Because of its great corrosive powers it was also called "*aqua fortis.*"

174. Preparation. Nitric acid is made by the action of strong sulfuric acid on sodium or potassium nitrate; manufacturing plants employ essentially the same process; sodium nitrate is used, as it is cheaper than potassium nitrate.

$$NaNO_3 + H_2SO_4 \rightarrow HNaSO_4 + HNO_3$$
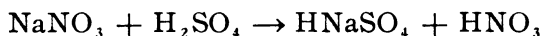
The nitric acid thus obtained is not pure; it is contaminated with nitrogen peroxid, which is shown by its yellow color. It is purified by distillation, yielding a distillate containing about 60 per cent of the pure acid. If carefully dried saltpeter and concentrated sulfuric acid be used, the nitric acid obtained is very nearly 100 per cent pure. If the heating is done under diminished pressure, the yield and the purity of the acid is increased.
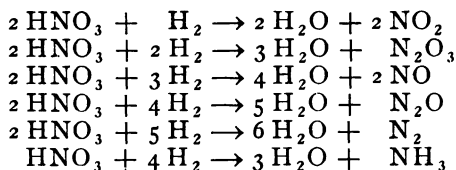
175. Properties. *Physical.* Pure nitric acid is a colorless liquid with a very pungent odor, miscible in all proportions with water.

Chemical. At a red heat nitric acid is decomposed into water, oxygen, and nitrogen peroxid; sunlight effects the same decomposition slowly. It is very corrosive; but few substances withstand its attack. It dissolves most metals, forming *nitrates*, all of which are soluble in water. It is a powerful oxidizing agent, and stains the nails and flesh yellow.

REDUCTION OF NITRIC ACID. When nitric acid acts upon metals, the hydrogen we might expect to be evolved at first in accordance with the equation:

$$\underset{(copper)}{Cu} + 2HNO_3 \rightarrow H_2 + \underset{(copper\ nitrate)}{Cu(NO_3)_2}$$
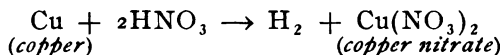
reacts with the acid, depriving it of some of its oxygen and forming certain of the oxids of nitrogen. These reactions may be shown by the following equations:

$$2\,HNO_3 + H_2 \rightarrow 2\,H_2O + 2\,NO_2$$
$$2\,HNO_3 + 2\,H_2 \rightarrow 3\,H_2O + N_2O_3$$
$$2\,HNO_3 + 3\,H_2 \rightarrow 4\,H_2O + 2\,NO$$
$$2\,HNO_3 + 4\,H_2 \rightarrow 5\,H_2O + N_2O$$
$$2\,HNO_3 + 5\,H_2 \rightarrow 6\,H_2O + N_2$$
$$HNO_3 + 4\,H_2 \rightarrow 3\,H_2O + NH_3$$

Which of these reactions will predominate depends upon the nature of the metals, the strength of the acid, the temperature, and on the amount of the nitrate of the metal which is already formed. For example, when copper is used, at first some nitrogen tetroxid is formed, then nitrogen dioxid and monoxid (only a little), and usually a very little nitrogen. During the course of the reaction several of these oxids may be simultaneously formed. By repeated trials, however, it has been ascertained what particular conditions must be observed in order to give a predominance to one oxid.

176. Fuming Nitric Acid. Nitrogen dioxid is quite soluble in nitric acid; the solution has a red color and gives off reddish fumes, whence the name.

Fuming nitric acid is prepared by heating to a high temperature potassium nitrate and sulfuric acid. All the hydrogen is thereby expelled from the sulfuric acid:

$$2\,NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HNO_3$$
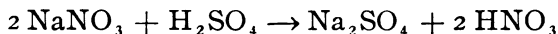
Much of the nitric acid dissociates, however, at this higher temperature, and the NO_2 dissolves in the distillate:

$$4\,HNO_3 \rightarrow 4\,NO_2 + 2\,H_2O + O_2$$
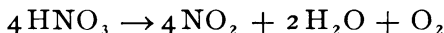
By virtue of the dissolved dioxid this acid has even a more powerful oxidizing action than pure nitric acid.

177. Uses. Nitric acid is used in making sulfuric acid, nitrobenzene, gun cotton, nitroglycerin, and celluloid. It is employed in etching on copper and in producing yellow patterns on woolen goods.

178. Nitrous Acid. Nitrous acid may be prepared by dissolving nitrogen trioxid or dioxid in water; nitric acid also is formed in the latter case,

and by the action of dilute sulfuric acid on a very dilute solution of sodium nitrite:

$$H_2SO_4 + 2\,NaNO_2 \rightarrow Na_2SO_4 + 2\,HNO_2$$
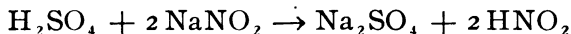
Nitrous acid is quite unstable, and is of no practical importance, although certain of its compounds with metals, such as sodium nitrite, are used in various experiments in the laboratory and in the manufacture of dyestuffs.

Exercises

1. How may oxygen and nitrous oxid be distinguished?

2. When ammonia and air are heated and passed over the catalytic agent (platinum sponge), nitric acid is formed. What does this prove as to the composition of nitric acid?

3. If nitric acid be boiled and its vapor passed through a tube containing red-hot copper, water and nitrogen pass out of the tube. What light does this fact throw upon the composition of nitric acid?

4. What happens to nitric acid when passed through a red-hot tube?

5. Why does even the purest of nitric acid turn yellow and even brown on standing in a lighted room?

6. What is the effect of heat upon (*a*) potassium nitrate? (*b*) lead nitrate? (*c*) ammonium nitrate?

Problems

1. How much nitric acid has to be decomposed in order to yield 100 *g.* of oxygen?

2. Turner, in 1833, obtained from 222.884 *g.* of silver nitrate, $AgNO_3$, 188.050 *g.* silver chlorid, AgCl. The atomic weights of silver, oxygen, and chlorin are 107.94, 16.00, and 35.45, respectively. What is the atomic weight of nitrogen?

3. Penny, in 1839, converted

   I. 291.439 *g.* $KClO_3$ into 240 553 *g.* KNO_3
   II. 420.064 *g.* KCl into 569.756 *g.* KNO_3
   III. 448.270 *g.* KNO_3 into 330.496 *g.* KCl

The atomic weights of potassium, chlorin, and oxygen are 39.14, 35.45, and 16.00, respectively. Calculate in each series of determinations the atomic weight of nitrogen.

PREPARATION AND PROPERTIES OF ACIDS, SALTS, AND BASES

A large number of the reactions which remain to be studied have to do with the preparation of salts, acids, and bases, and it is accordingly well to give a preliminary account of the general principles governing such preparations. In most of the methods employed the compounds are obtained in solution, and to obtain them in a state of purity the water has to be removed by evaporation and the compounds, when they are solid, crystallized out.
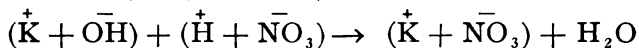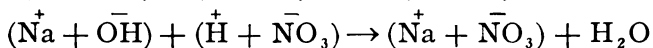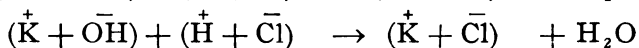
PREPARATION OF SALTS

179. By Direct Union of Elements. Many metals unite directly with non-metals to form salts. Thus, if chlorin be passed over sodium, common table salt (sodium chlorid) is produced; mercury, iron, and other metals also combine directly with the halogens. Many metals "burn" in chlorin gas with almost as much brilliancy as in oxygen.

180. By Action of an Acid on a Metal. Many soluble salts may be prepared by dissolving a metal in an acid. The metal combines with the anion of the acid, forming the salt which remains dissolved. Insoluble salts cannot usually be made in this way, for the salt which may be produced when the metal and acid are first brought together, forms a coating over the metal, thus protecting it from further

action. Besides the salt, hydrogen is also produced, and this may react with the acid to give rise to other substances. Thus, nitric acid is reduced by metals (§ 175), as is also the case with strong sulfuric acid, but with no evolution of hydrogen.

181. By Action of an Acid on a Base; Neutralization. When solutions of an acid and of a base are brought together the anion of the acid combines with the cation of the base to form a salt, while the hydrogen of the acid and the hydroxyl of the base unite to form water.

According to the theory of electrolytic dissociation a soluble acid or base is more or less dissociated into its ions by the very act of solution. When a solution of an acid is mixed with a solution of a base, since both the compounds are already ionized, the mixing would merely affect the degree of ionization. As water, however, dissociates but very slightly into its ions, $\overset{+}{H}$ and $\overset{-}{OH}$, the hydrogen and hydroxyl ions contained in the acid and base unite to form water, when the solutions are mixed, and the main chemical reaction in neutralization is the formation of water. The equations for a number of neutralization reactions are the following:

$$(\overset{+}{Na} + \overset{-}{OH}) + (\overset{+}{H} + \overset{-}{Cl}) \rightarrow (\overset{+}{Na} + \overset{-}{Cl}) + H_2O$$
$$(\overset{+}{K} + \overset{-}{OH}) + (\overset{+}{H} + \overset{-}{Cl}) \rightarrow (\overset{+}{K} + \overset{-}{Cl}) + H_2O$$
$$(\overset{+}{Na} + \overset{-}{OH}) + (\overset{+}{H} + \overset{-}{NO_3}) \rightarrow (\overset{+}{Na} + \overset{-}{NO_3}) + H_2O$$
$$(\overset{+}{K} + \overset{-}{OH}) + (\overset{+}{H} + \overset{-}{NO_3}) \rightarrow (\overset{+}{K} + \overset{-}{NO_3}) + H_2O$$
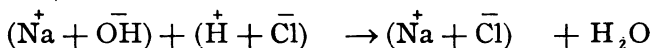
Many more similar equations could be written, but enough are probably given to show the mechanism

of the reaction. The left members always contain hydrogen and hydroxyl ions together with the cation of the base and the anion of the acid. In the right member the latter remain unchanged, while the hydrogen and hydroxyl ions unite to form water.

If in the phenomenon of neutralization the chief chemical action is the formation of water, the energy changes due to neutralization should be the same when such quantities of acid and base are used as produce equal amounts of water. And this deduction has been found to be true.

182. By Action of an Acid on Salts. Examples of this reaction have been discussed on page 78, and others will be considered later. A favorite salt is the carbonate, as the carbon dioxid produced is gaseous and therefore easily separated from the salt desired. Thus, the reaction between calcium carbonate (marble) and hydrochloric acid to give calcium chlorid, $CaCl_2$, carbon dioxid, and water may be represented by the equation:

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O$$
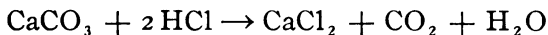
PREPARATION OF ACIDS

183. General Method. The general method of preparation of an acid consists in heating a salt with another acid of higher boiling point. Sulfuric acid is less volatile than most other acids, and hence usually employed. The oxids of the non-metals, as sulfur and phosphorus, react with water to produce acids.

"STRENGTH" OF AN ACID. The true measure of the "strength" of an acid is not its ability to displace

another acid from a salt, when the first acid and the salt are heated together, for that ability depends almost wholly upon the relative volatility of the two acids. The true measure of the "strength" of acids is rather their degree of ionization in solution. Under like conditions of dilution, sulfuric acid is only about half as much ionized as either nitric or hydrochloric acid, and hence is really but about half as "strong."

PREPARATION OF BASES

184. Soluble Bases. Soluble bases may be made by the action of slaked lime or caustic alkalis on certain salts of the base required. General rules can hardly be given; each case must be considered by itself.

185. Insoluble Bases. Insoluble bases are prepared by mixing two solutions, one of which contains hydroxyl ions and the other cations of the base desired. Thus, the insoluble base, iron hydroxid, $Fe(OH)_2$, can be prepared by adding a solution of potassium hydroxid, KOH, to a solution of iron sulfate, $FeSO_4$, although any other iron (ferrous) soluble salt would do as well and any other soluble hydroxid.

HYDROLYSIS. A number of salts are known which have a basic or acid reaction in solution. All such salts are made up of a strong base combined with a weak acid or a weak base combined with a strong acid. Now the strength of a base or of an acid depends upon its degree of ionization. When a salt made up of a strong base and a weak acid is dissolved in water, although there are some hydrogen ions present, the number of hydroxyl ions is so much larger that the solution as a whole shows a basic behavior and gives an alkalin reaction. Likewise, a salt composed of a weak base and a strong acid is dissociated into so many more hydrogen than hydroxyl ions that its reaction is acid.

THE HALOGENS; THEIR HYDROGEN AND OXYGEN COMPOUNDS

The name "halogen" (from two Greek words, meaning *salt-producer*) is given to the closely related group of elements, fluorin, chlorin, bromin, and iodin, because these elements combine directly with many metals to form compounds known as *halid salts*, or simply *halids*.
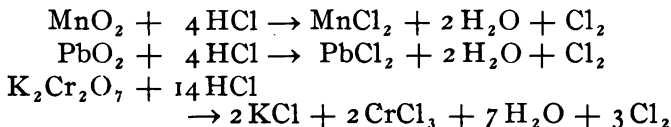
CHLORIN

HISTORICAL NOTE. Free chlorin was first obtained by Scheele in 1774 by heating hydrochloric acid with manganese dioxid. A little later, Berthollet observed that its aqueous solution gave off oxygen when exposed to sunlight, and he therefore drew the erroneous conclusion that chlorin contains oxygen. In 1810, however, Davy proved the absence of oxygen in the substance, and Gay-Lussac, who also independently arrived at the same conclusion, gave the name of chlorin (from a Greek word, meaning *green*) to the new element.

186. Occurrence. Free chlorin is not met with in nature. Its compounds with sodium, potassium, and magnesium are very abundant, however, forming the larger part of the residue left after the evaporation of sea water. The beds of dried-up seas and lakes, therefore, consist largely of chlorin salts.

187. Preparation. A compound rich in oxygen, as manganese dioxid, MnO_2, lead dioxid, PbO_2, potassium dichromate, $K_2Cr_2O_7$, or potassium chlorate, $KClO_3$, is heated with hydrochloric acid. The acid is oxidized, its hydrogen unites with the oxygen

to form water, and a part of the chlorin is set free; the rest of the chlorin combines with the metal to form a salt:

$$MnO_2 + 4\,HCl \rightarrow MnCl_2 + 2\,H_2O + Cl_2$$
$$PbO_2 + 4\,HCl \rightarrow PbCl_2 + 2\,H_2O + Cl_2$$
$$K_2Cr_2O_7 + 14\,HCl$$
$$\rightarrow 2\,KCl + 2\,CrCl_3 + 7\,H_2O + 3\,Cl_2$$

Instead of first preparing hydrochloric acid and then letting it react with the oxidizing agent, the hydrochloric acid may be formed by the reaction of sulfuric acid on salt, which, as soon as it is formed, is oxidized by the oxidizing agent, usually manganese dioxid:

$$MnO_2 + 2\,H_2SO_4 + 2\,NaCl$$
$$\rightarrow MnSO_4 + 2\,H_2O + Na_2\,SO_4 + Cl_2$$
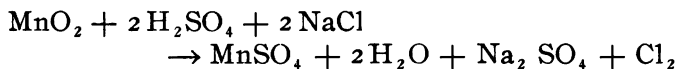
Chlorin may also be obtained by the action of strong hydrochloric acid on bleaching powder, and by the electrolysis of some metallic chlorid, such as sodium chlorid; graphite electrodes are used, since chlorin attacks metallic ones.

188. Manufacture Chlorin gas is used in several industries in large amounts. Several technical processes have been devised to utilize in a more or less direct manner the oxygen of the air to effect the oxidation of hydrochloric acid.

Deacon's Process. A mixture of hydrogen chlorid, HCl, and air is conducted through heated tubes filled with fragments of burnt clay impregnated with some salt of copper. The copper salt acts catalytically so that steam and chlorin pass out of the tubes. The reaction is not well understood, but it really amounts to an oxidation of hydrogen chlorid:

$$4\,HCl + O_2 \rightarrow 2\,H_2O + 2\,Cl_2$$
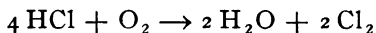
As air contains nitrogen, the chlorin thus obtained is mixed with about 70 per cent of that gas, which, however, is of little moment in many industrial applications.

WELDON PROCESS. The soluble manganous chlorid, $MnCl_2$, which is formed when manganese dioxid acts on hydrochloric acid, is treated with slaked lime :

$$MnCl_2 + Ca(OH)_2 \rightarrow CaCl_2 + Mn(OH)_2$$
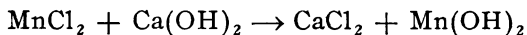
Soluble calcium chlorid, $CaCl_2$, and insoluble manganous hydroxid, $Mn(OH)_2$, are produced. A current of air is forced through the mixture whereby the manganous hydroxid is oxidized to manganous acid :

$$2 Mn(OH)_2 + O_2 \rightarrow 2 H_2MnO_3$$
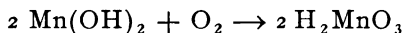
The manganous acid combines with the calcium hydroxid present to form insoluble calcium manganite :

$$H_2MnO_3 + Ca(OH)_2 \rightarrow CaMnO_3 + 2 H_2O$$
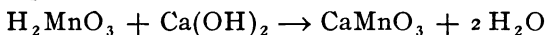
The calcium manganite is filtered and treated with hydrochloric acid ; chlorin is thus obtained :

$$CaMnO_3 + 6 HCl \rightarrow MnCl_2 + CaCl_2 + 3 H_2O + Cl_2$$
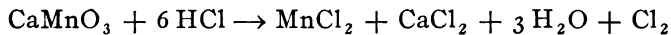
The manganous chlorid is thus seen to be regenerated and can again be subjected to the same process as above. It is also apparent that the oxidation is effected by atmospheric oxygen. A disadvantage of the method is the loss of about two-thirds of the chlorin in the hydrochloric acid, for the calcium chlorid which is formed is almost valueless.

MAGNESIUM CHLORID PROCESS. Magnesium chlorid occurs in considerable quantities in the mineral carnallite, $MgCl_2 \cdot KCl$, and is also obtained from other sources. When heated with steam it yields hydrochloric acid :

$$MgCl_2 + H_2O \rightarrow MgO + 2 HCl$$
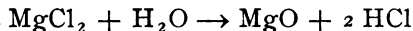
When heated in the absence of water in a current of air, it gives chlorin :

$$2 MgCl_2 + O_2 \rightarrow 2 MgO + 2 Cl_2$$
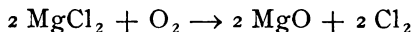
ELECTROLYTIC PROCESSES. Both in Castner's and in Acker's electrolytic methods of manufacturing sodium hydroxid (page 187) chlorin is evolved at one pole.

189. Properties. *Physical.* (Table I., Appendix *D.*) Chlorin is a greenish-yellow gas with a very disagreeable smell. It is soluble in about a third of its volume of water.

Chemical. Chlorin combines directly with all but some rare elements and oxygen, nitrogen, carbon, and fluorin, although by indirect methods compounds of the elements specified can be obtained. Hydrogen and chlorin do not combine at low temperatures and in the dark; they do so, however, at high temperature, and with explosive violence when exposed to sunlight. Hydrogen, as well as many metals, "burn" in the gas. Aqueous solutions decompose slowly when exposed to light; the hydrogen combines with the halogen to form hydrochloric acid, and the oxygen is set free. Chlorin in the presence of water acts then as an oxidizing agent, for the oxygen set free acts upon other substances present.

OTHER REACTIONS OF CHLORIN. Chlorin acts upon a large number of hydrocarbons. Thus, methane reacts with chlorin to form methane chlorid, more commonly called methyl chlorid or chlor-methane:

$$CH_4 + Cl_2 \rightarrow HCl + CH_3Cl$$
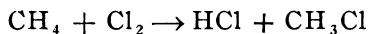
Chlor-methane, when acted on afresh by chlorin, gives di-chlor-methane, CH_2Cl_2, thus:

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$
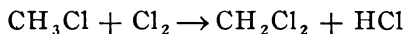
Similarly, tri-chlor-methane, $CHCl_3$, commonly called chloroform, and tetra-chlor-methane, CCl_4, may be formed by the further action of chlorin. Such reactions as these where one element is substituted for another are very common among the compounds of carbon, and are called *substitution reactions.*

BLEACHING. Most textile fabrics, such as linen and cotton, naturally have a yellow tinge, and the object of

bleaching is to remove this color. Formerly the fabrics were spread out on the grass and kept moist: The oxygen given off by the grass which, like all green plants under the action of sunlight, absorbs carbon dioxid and gives off oxygen, bleached the cloths. This process, although effectual, is slow and expensive. Hence, soon after the discovery of chlorin and its properties, it was applied in bleaching. Gaseous chlorin, however, is not ordinarily used because of the difficulty of manipulating it, but a solid compound which, under proper conditions, readily gives off chlorin, is used instead. The commonest of these compounds is bleaching powder, made from slaked lime and chlorin. It is really not the chlorin which does the bleaching, but the oxygen which the chlorin liberates from water. This we know, because dry chlorin will not bleach at all. Bleaching is, therefore, a process of oxidation, the products of which are colorless. In this bleaching, chlorin soon attacks and destroys the fiber of the cloth. For this reason it is not in favor among laundresses ; they prefer to mask the yellowness of the washed cloth by the addition of "bluing," since blue and yellow, being complementary colors, appear white when mixed. Manufacturers, to counteract the injurious action of chlorin after the bleaching is accomplished, use certain substances called "antichlors," which form harmless compounds with the excess of the chlorin.

LIQUID CHLORIN. When a solution of chlorin in water is cooled or chlorin is passed into ice-cold water, yellow crystals are formed, which have a composition corresponding to the formula, $Cl_2 \cdot 10\,H_2O$. This *chlorin hydrate* breaks up into chlorin and water when heated, and Faraday made use of this compound in first liquefying the element in 1823, according to the method described under Ammonia (page 65).

Liquid chlorin is bright yellow, and solidifies at temperatures below $-102°$. It is used commercially and is stored and shipped in steel cylinders lined with lead.

190. Uses. Chlorin is used in making bleaching powder, chlorates, chloroform, and also in gold mining.

FLUORIN

191. Preparation and Properties. It had long
been suspected that certain minerals contained an
element resembling chlorin, but all attempts to iso-
late it had failed until Moissan in 1886 subjected
its hydrogen compound, hydrofluoric acid, HF, to
electrolysis conducted at low temperatures in plati-
num vessels. Fluorin is a lemon-colored gas of
very penetrating and disagreeable odor. It is
extremely active chemically, combining with most
other elements; oxygen is a notable exception.
It decomposes water instantly, forming hydro-
fluoric acid, HF, and oxygen mixed with ozone.

BROMIN

HISTORICAL NOTE. Bromin was discovered in 1826
by Balard, who treated the liquor left after the crystalliz-
ing of the common salt from a salt spring with a mixture
of manganese dioxid and strong sulfuric acid. He gave
it the name of bromin, derived from the Greek word
for stench.

192. Occurrence. Bromin never occurs free,
but its compounds with sodium, potassium, mag-
nesium, and several other metals occur in small
amounts in sea water and some mineral springs.
Small quantities of silver bromid, AgBr, occur in
some Mexican mines, and bromids in minute pro-
portion are found in connection with Chile salt-
peter, $NaNO_3$.

193. Preparation. Bromin is freed from com-
bination either by heating bromids with sulfuric
acid and manganese dioxid, or by decomposing
them with free chlorin. In both methods the sea
or salt spring water is first concentrated so that the

chlorids which are also present and are less soluble than the bromids may crystallize out. The crystals are removed from the residual liquor or "mother liquor," which is named "bittern." In the *continuous process* the hot bittern is allowed to trickle down through a tall tower filled with clay balls so as to meet an ascending current of chlorin gas which sets the bromin free and itself combines with the metals. The bromin dissolves in the solution and is collected in a cistern at the base of the tower. In the *periodic process* a stoneware still is charged with bittern, manganese dioxid, and sulfuric acid. This mixture is heated by steam and the bromin which is given off is condensed.

194. **Properties.** *Physical.* (Table I., Appendix *D.*) Bromin is a dark red, volatile liquid of strong and disagreeable smell; it has a very irritating action on the eyes. It is about three times as heavy as water, a liter of which dissolves about thirty-five grams.

Chemical. Bromin combines with nearly all the elements; oxygen is the chief exception. Its action toward metals is like that of chlorin, but less intense. A mixture of bromin vapor and hydrogen has to be heated to cause combination. Bromin decomposes water slowly, even in darkness, and hence may act as an oxidizing agent in a fashion similar to chlorin. Water and bromin, when cold, form *bromin hydrate*, $Br_2 \cdot 10 H_2O$, similar to chlorin hydrate.

195. **Uses.** Bromin is employed in the manufacture of anilin colors, and of certain of its salts. Silver bromid is a constituent of many kinds of photographic plates and paper.

IODIN

HISTORICAL NOTE. The ashes of some seaweeds, called *kelp*, were formerly employed in making sodium carbonate (washing soda), and Courtois, in 1811, on examining the mother liquor from which the carbonate had crystallized, discovered a new substance which he turned over to Gay-Lussac for investigation. Davy also examined the same substance at about the same time. They both proved it to be a new element, and it was given the name of "iodin" (the Greek word for violet color) because its vapor is violet.

196. Occurrence. Iodin does not occur free. Small amounts of its compounds with the metals potassium and sodium are found associated with many other substances. The principal sources of these iodids are kelp and Chile saltpeter.

197. Preparation. Sodium iodid, NaI, is separated from Chile saltpeter and purified by repeated crystallizations. It is then dissolved and a current of chlorin gas passed into the solution. Sodium chlorid is formed and the iodin precipitated as a black powder. Or the mother liquor from kelp is treated with chlorin as above, or gently heated with sulfuric acid, with the addition of small quantities of manganese dioxid from time to time until all the iodin is liberated. Just enough manganese dioxid is added to free the iodin; an excess is avoided, as it would cause the liberation of the bromin in the bromids accompanying the iodids. The iodin resulting from both processes is purified by sublimation.

198. Properties. *Physical.* (Table I., Appendix *D*.) Iodin is a heavy, grayish-black solid with metallic luster, and an odor resembling that of bromin, but less penetrating. It vaporizes slowly at ordinary

temperatures, and when heated turns into a vapor of a dark violet color. It stains the skin, paper, etc., brown. It is but slightly soluble in water, giving a solution brown in color, but it is quite soluble in ether and carbon bisulfid, yielding violet solutions. It also forms a colorless solution in an aqueous solution of potassium iodid.

Chemical. Iodin combines with most of the elements forming iodids; it does not burn, but by an indirect method may be made to combine with oxygen to form iodin pentoxid, I_2O_5, a white powder. It combines very vigorously with phosphorus. Nitrogen iodid, NI_3, a compound of iodin and nitrogen, explodes at the slightest shock, even at the touch of a feather.

199. Uses. A solution of iodin in alcohol, which is known as "tincture of iodin," is used as an external application in medicine. Iodin enters into the composition of iodoform, a surgical dressing, and large amounts of the element are used in making certain anilin dyes.

COMPOUNDS OF THE HALOGENS WITH HYDROGEN; THE HYDRACIDS

200. In General. One volume of each of the halogens, when in the state of vapor, combines with an equal volume of hydrogen gas to give two volumes of a gaseous compound:

$$F_2 \text{ or } Cl_2 \text{ or } Br_2 \text{ or } I_2 + H_2 \rightarrow$$
$$2\,HF \text{ or } 2\,HCl \text{ or } 2\,HBr \text{ or } 2\,HI$$
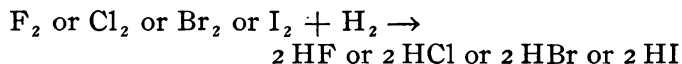
When dissolved in water these hydrogen compounds form strong acids, often called *hydracids;*

their individual names are hydrofluoric acid, HF, hydrochloric acid, HCl, hydrobromic acid, HBr, and hydriodic acid, HI. They are also called, when in the gaseous state, hydrogen or hydric fluorid, chlorid, bromid, and iodid, respectively.

The physical and chemical properties of these compounds are very similar. They are all colorless gases with sharp, suffocating odor and acid taste, and are very soluble in water. They dissociate into their elements at high temperatures.

HYDROCHLORIC ACID

HISTORICAL NOTE. Hydrochloric acid was known to the ancients, who prepared it by heating a mixture of common salt, iron pyrites, and clay. Glauber, in the seventeenth century, substituted oil of vitriol for the clay and pyrites, but it was not until the end of the eighteenth century that Cavendish obtained it in the gaseous state and that Priestley studied its properties. It was formerly called "spirits of salt" and "muriatic acid."

201. Occurrence. Hydrochloric acid sometimes exists in volcanic gases and is occasionally found in rivers whose sources are in volcanic regions.

202. Preparation. Common salt is heated with sulfuric acid. When one molecule of sodium chlorid reacts with one molecule of sulfuric acid, only one hydrogen atom is removed from the molecule of the acid, and acid or hydrogen sodium sulfate, $NaHSO_4$, is formed, while if the proportion of salt be doubled, normal sodium sulfate, Na_2SO_4, is produced; the latter reaction occurs at a higher temperature than the former. The equations are:

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$
$$2\,NaCl + H_2SO_4 \rightarrow 2\,HCl + Na_2SO_4$$
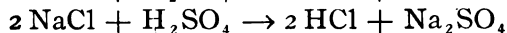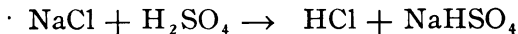
203. Properties. *Physical.* The aqueous solution of hydrogen chlorid distils at 110°; the distillate contains about 20 per cent of HCl.

Chemical. Hydrogen chlorid does not support ordinary combustion, but sodium and potassium, if ignited and then introduced into the gas, will continue to burn with great vigor; hydrogen is set free and chlorids of the metals are formed. Hydrogen chlorid dissociates at high temperatures, and electric sparks effect the same result slowly.

Composition. If a given volume of hydrogen chlorid be enclosed in a tube containing a little sodium or aluminum, and the metal be heated, there ensues a diminution of one-half in volume, and the residual gas is hydrogen. Similarly, if a little manganese dioxid be heated in a closed tube filled with hydrogen chlorid, there is a diminution in volume amounting to one-half, and the gas remaining is chlorin. Hydrogen chlorid therefore consists of equal volumes of hydrogen and chlorin.

204. Uses. Hydrogen chlorid is employed in preparing chlorin by Deacon's process, and in solution for the same purpose in Scheele's and Weldon's processes. Hydrochloric acid is used in medicine, and in the manufacture of gelatin.

HYDROFLUORIC ACID

Historical Note. The fact that a mixture of the mineral fluorspar (calcium fluorid, CaF_2) and oil of vitriol (sulfuric acid), when gently heated, gives off vapors which attack glass, was known and utilized in the etching of glass in the seventeenth century, but it was not until 1771 that Scheele succeeded in isolating the gas.

205. Preparation and Properties. Calcium fluorid is pulverized and heated with strong sulfuric acid, best in a leaden vessel.

$$CaF_2 + H_2SO_4 \rightarrow 2\,HF + CaSO_4$$
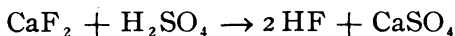
Hydrogen fluorid combines with the silicon in glass to form a volatile fluorid of silicon, SiF_4. As it attacks glass, its solution has to be stored in gutta-percha or lead bottles. This property of attacking glass is utilized in the manufacture of graduated glass vessels, such as burettes and pipettes.

HYDROBROMIC ACID

206. Preparation and Properties. Hydrobromic acid cannot be prepared by the action of concentrated sulfuric acid on a metallic bromid, as strong, hot sulfuric acid decomposes it. If the acid be diluted with about a third its volume of water, however, and a gentle heat applied, hydrogen bromid is generated. The bromids of phosphorus are decomposed by water, yielding hydrobromic acid. A current of hydrogen sulfid, H_2S, when passed into a solution of bromin in water, is decomposed into sulfur and hydrogen; the latter unites with the bromin to give a solution of the acid.

$$H_2S + Br_2 \rightarrow 2\,HBr + S$$
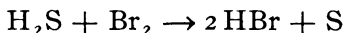
A very convenient method consists in letting bromin fall drop by drop on naphthalene (moth balls) contained in a retort. A bromid of naphthalene is formed and the hydrogen bromid given off is absorbed by the water.

Hydrogen bromid, in most of its physical and chemical properties, resembles hydrogen chlorid. It is a colorless gas with a sharp odor and a very acid taste. It is extremely soluble in water, and the solution thus formed, if saturated with the gas,

fumes on coming in contact with the air. Hydrobromic acid attacks most metals with evolution of hydrogen and formation of a metallic bromid.

HYDRIODIC ACID

207. Preparation and Properties. Hydriodic acid is usually prepared by the action of water on phosphorus iodid or by the action of hydrogen sulfid on iodin suspended in water.

Hydriodic acid has properties similar to those of the other hydracids. It is decomposed by both bromin and chlorin, which combine with its hydrogen to form corresponding hydracids, and set the iodin free. Hydrogen iodid dissociates at about 400°.

### OXYGEN COMPOUNDS OF THE HALOGENS

No oxids or oxygen-containing acids of fluorin are known. Chlorin forms three oxids: chlorin monoxid, Cl_2O; chlorin dioxid, ClO_2; and chlorin trioxid, Cl_2O_3. They are all heavy, greenish gases, and quite unstable. Four oxygen acids of chlorin are known: hypochlorous acid, $HClO$, which is itself unstable, but gives certain important salts, as calcium hypochlorite, $CaCl_2O_2$, the active constituent of bleaching powder; chlorous acid, $HClO_2$, which may be prepared by dissolving chlorin trioxid in water; chloric acid, $HClO_3$, which is a strong oxidizing agent and when heated breaks up into oxygen and perchloric acid, $HClO_4$.

No oxids of bromin have been prepared, but the two oxygen acids, hypobromous acid, $HBrO$, and bromic acid, $HBrO_3$, are known.

Two oxids of iodin exist: iodin tetroxid, I_2O_4, and pentoxid, I_2O_5; also two oxygen acids are known: iodic acid, HIO_3, and periodic acid, HIO_4. All four compounds are white crystalline solids soluble in water.
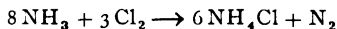
Exercises

1. How can chlorin readily be distinguished from all other gases thus far studied?

2. What are the chemical reactions involved in the etching of glass?

3. Of the properties of chlorin, which is the most valuable commercially?

4. How can you separate iodin from sand in two different ways?

5. Why is it so difficult to isolate fluorin?

6. Write the equation for the interaction of:

$$(a)\ H_2SO_4,\ MnO_2,\ KBr$$
$$(b)\ H_2SO_4,\ MnO_2,\ KI$$
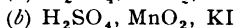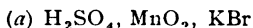
Problems

1. Chlorin reacts with ammonia according to the equation:

$$8\,NH_3 + 3\,Cl_2 \longrightarrow 6\,NH_4Cl + N_2$$

How many liters of nitrogen may be obtained by the action of chlorin on 10 *l.* of ammonia? How many liters of chlorin will be required?

2. If the weight of one liter of hydrogen chlorid, HCl, is 1.735*g.*, what is the elemental weight of chlorin?

3. How much potassium is needed to prepare 63.5 *g.* of iodin?

4. Hydrogen and chlorin were mixed and exploded; the hydrogen chlorid produced weighed 14.6 *g.* What were the weights and volumes of the hydrogen and chlorin used?

5. How many grams of chlorin can be obtained, theoretically, by the electrolysis of 100 *g.* of hydrochloric acid?

6. How many grams of sodium chlorid are required to prepare a kilogram of hydrogen chlorid?

7. A room 6 *m.* long, 5 *m.* wide, and 3.5 *m.* high was disinfected with chlorin; enough was used to make 0.15 per cent by volume of the air present. How many grams of chlorin were required?

8. How many liters of hydrogen at 20° and 773 *mm.* can be obtained by the action of an excess of zinc upon 25.0 *g.* of hydrochloric acid?

9. How much chlorin can be obtained from the oxidation of 1,000 *g.* of hydrochloric acid?

10. Dumas, in 1859, heated 12.034 *g.* of silver bromid in an atmosphere of chlorin and obtained 9.185 *g.* of silver chlorid. If the atomic weight of chlorin is 35.45, what is that of bromin?

11. The analysis of a certain compound gave the following results:

	I	II	III
C =	12.00%	11.69%	11.83%
H =	3.98%	4.02%	4.00%
N =	6.77%	6.80%	6.78%
Br =	77.56%	77.61%	77.64%

What is its formula?

12. Marignac, in 1843, converted 100.000 parts of silver into 174.065 parts of silver bromid. The atomic weight of silver is 107.94; what is that of bromin?

13. Marignac, in 1843, heated potassium bromate, $KBrO_3$, and obtained 71.277% of potassium bromid, KBr. The atomic weights of potassium and oxygen are 39.14 and 16.00, respectively; what is that of bromin?

14. Ladenburg, in 1902, heated 63.8351 *g.* of silver iodid in a current of chlorin and obtained 38.9656 *g.* of silver chlorid. The atomic weights of silver and chlorin are 107.94 and 35.45, respectively; what is the atomic weight of iodin?

15. De Luca, in 1862, by repeatedly evaporating to dryness 2.6670 *g.* of fluorspar, CaF_2, with sulfuric acid obtained 4.6590 *g.* of calcium sulfate. If the atomic weights of calcium, sulfur, and oxygen are 40.0, 32.06, and 16.00, respectively, what is that of fluorin?

16. The specific gravity of chlorin referred to hydrogen is nearly 36. Compare its speed of diffusion with that of hydrogen.

17. If hydrochloric acid contains 2.7 per cent of hydrogen, how many liters of hydrogen at 93° and 265 *mm.* can be obtained from 38 *g.* of the acid?

18. How many grams of manganese dioxid are required to prepare 100 *g.* of chlorin from hydrochloric acid?

19. A saturated solution of chlorin when exposed to sunlight yielded 20 *c.c.* of a gas. How would you establish the identity of this gas, and how much chlorin was required to produce it?

CHAPTER XVIII

THE ALKALI METALS

208. In General. The metals *lithium, sodium, potassium, rubidium,* and *cæsium* constitute a family of very similar elements, many of whose compounds are of great practical importance. They are all silvery-white metals, so soft as to be easily cut with a knife, rapidly tarnish when exposed to moist air, decompose water at ordinary temperatures, and burn when heated in the air. Their salts, with hardly an exception, are soluble in water. Both their physical and chemical properties vary regularly with their atomic weights from element to element, and they are all univalent.

ELEMENT	*Symbol*	*Atomic weight*	*Density*	*Melting point*	*Boiling point*
Lithium	Li	7.03	0.59	180°	red heat
Sodium	Na	23.05	0.974	95.6	742°
Potassium	K	39.15	0.875	62.5	667
Rubidium	Rb	85.4	1.522	38.5	....
Cæsium	Cs	133	1.85	26.5	270

HISTORICAL NOTE. The word *alkali* was at first applied to the caustic liquor obtained by the leaching of wood ashes, and to distinguish it from the caustic liquor containing ammonium carbonate known as *volatile alkali*, it was named *fixed alkali*. Later a distinction into *mineral fixed alkali* and *vegetable fixed alkali* was made, as it was believed that what we now call caustic soda was entirely of mineral origin, while caustic potash was of vegetable origin. The fixed alkalis were held to be elementary in nature, but Lavoisier thought

that "these substances are evidently compounds, although we are as yet ignorant of the nature of the principles entering into their composition." Davy in 1807 succeeded in isolating potassium and sodium by electrolysis of their fused hydroxids; lithium was discovered in 1817, and rubidium and cæsium in 1860.

209. Lithium. Lithium is widely distributed, but always in small amounts. It is prepared by the electrolysis of its chlorid either fused or dissolved in pyridin. It tinges the Bunsen flame crimson.

SODIUM AND POTASSIUM

210. Occurrence. Sodium and potassium occur only in compounds. United with oxygen, silicon, and aluminum, they are found in especially great abundance in feldspar and mica. Common salt (sodium chlorid, $NaCl$) is found in sea water, salt lakes, or as the mineral rock salt or *halite*. Sea water contains about 3 per cent of salt, while some salt lakes contain as much as 30 per cent, so that their waters are nearly saturated with it. *Sylvite* (potassium chlorid, KCl) and *carnallite*, $KCl \cdot MgCl_2$, are the principal minerals containing potassium. Potassium nitrate (niter or saltpeter), KNO_3, was first found as an incrustation in certain caves, whence the name saltpeter (salt from a rock). Chile saltpeter, or sodium nitrate, $NaNO_3$, forms great beds in Chile. Both nitrates are formed by the action of certain microörganisms on decaying animal and vegetable matter.

211. Preparation. Sodium and potassium can be obtained by electrolyzing certain of their compounds either in solution or fusion. They may also be obtained by heating their hydroxids with

charcoal. An intimate mixture of potassium carbonate and charcoal is placed in a retort connected with an iron receiver from which the air is excluded. At a high temperature the carbonate is reduced with formation of potassium and carbon monoxid:

$$K_2CO_3 + 2C \rightarrow 2K + 3CO$$
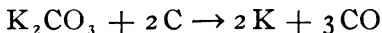
The metal distils over into the receiver and is collected under petroleum. Sodium hydroxid is melted and run into a highly heated mass of coke in a retort:

$$2NaOH + C \rightarrow H_2O + CO + 2Na$$

212. Properties. *Physical.* (Table I., Appendix *D.*) Sodium and potassium are so soft that they can be cut easily with a knife. The freshly cut surfaces have a bright metallic luster, soon tarnished, however, by the action of the water vapor in the air. They are lighter than water.
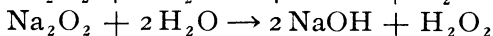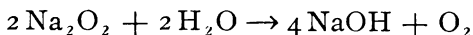
Chemical. Both sodium and potassium combine eagerly with oxygen and many other elements. When placed upon water they unite with a portion of it, forming the hydroxids, NaOH and KOH, and setting half the hydrogen free. So much heat is liberated that, in the case of potassium, the escaping hydrogen is set on fire; with sodium this occurs only when the water is hot. As they speedily unite with the oxygen and water vapor of the air, they have to be protected from its action; this is usually done by keeping them under naphtha or kerosene. They are very energetic reducing agents, and unite readily with the halogens. Their compounds impart characteristic colors to a Bunsen flame—potassium, violet, and sodium, yellow.

AMALGAMS. The alkali metals, when placed in warm mercury, dissolve with a flash of light and the evolution of much heat. The resulting *amalgams* are liquid when they contain less than 5 per cent of the alkali metal, but are dark gray solids when they contain more. Many other metals also form amalgams with mercury, but iron and platinum are notable exceptions. Amalgams are not true compounds, but are mixtures or solutions.

213. Ammonium. The radical, NH_4, has been found to form compounds similar to those of the alkali metals. The radical cannot, indeed, exist alone, but it forms an amalgam with mercury.

OXIDS AND HYDROXIDS OF THE ALKALI METALS

214. Oxids. Sodium and potassium burn in oxygen or nitrous oxid, forming several oxids, of which the most important are the *peroxids*, Na_2O_2 and KO_2, which are yellow solids reacting with water to give oxygen and the respective hydroxids. At low temperatures and with an excess of water, hydrogen dioxid is also formed.

$$2\,Na_2O_2 + 2\,H_2O \rightarrow 4\,NaOH + O_2$$
$$Na_2O_2 + 2\,H_2O \rightarrow 2\,NaOH + H_2O_2$$
$$K_2O_4 + 2\,H_2O \rightarrow 2\,KOH + H_2O_2 + O_2$$

HYDROXIDS

215. Preparation. Both sodium and potassium hydroxids were formerly made by the action of slaked lime (calcium hydroxid, $Ca(OH)_2$) on solutions of their carbonates, Na_2CO_3 and K_2CO_3.

Na_2CO_3 or $K_2CO_3 + Ca(OH)_2$
$$\rightarrow 2\,NaOH \text{ or } 2\,KOH + CaCO_3$$
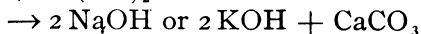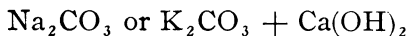
The insoluble calcium carbonate is removed by filtration and the solution evaporated to dryness.

The resulting "caustic soda," or "potash by lime," contains impurities which are insoluble in alcohol, and, to remove them, the mass is treated with alcohol. The alcoholic solution is filtered off and evaporated first in iron and then in silver vessels. After the alcohol has been driven off, the molten alkali is cast in silver molds; the product is known as "soda" or "potash by alcohol." A still purer grade of the alkalin hydroxids is prepared by dissolving the alkali metals in water and evaporating the resulting mixture to dryness.

ELECTROLYTIC PROCESSES. In the *Acker Process* melted sodium chlorid is electrolyzed in a large cast-iron vessel; the anode consists of several graphitized carbon blocks and the cathode of a layer of molten lead upon which the sodium chlorid floats. The resistance which the electrolyte offers to the passage of the current (which is very strong) changes enough of the electrical energy into heat energy to keep the salt at a temperature about 75° above its melting point (850°). Chlorin which is evolved at the anode is conducted over slaked lime, with which it reacts to form chlorid of lime. The sodium forms an alloy with the lead, which is decomposed by blowing a jet of steam into it, whereby caustic soda and hydrogen are formed; the latter is burned as soon as evolved.

In *Castner's Process* a solution of sodium chlorid is electrolyzed in an ingeniously devised cell in which the sodium on separating out forms an amalgam with some mercury present in the cell. This amalgam is automatically transferred to another part of the cell containing iron cathodes, where the water acts upon it; hydrogen is set free with the formation of sodium hydroxid.

216. Ammonium Hydroxid. Ammonium hydroxid is made by dissolving ammonia in water (§ 73). When boiled, the ammonia escapes; hence it is sometimes called the "volatile alkali."

217. Properties and Uses. Sodium and potassium hydroxids are white, brittle solids of disagreeable taste and are very soluble in water. They absorb carbon dioxid from the air, forming the corresponding carbonates, and are very deliquescent. They are powerful solvents of animal and vegetable substances, and are hence said to be "caustic." They are used in immense quantities in soap-making and many other industries.

218. Ammonium Hydroxid. Ammonium hydroxid resembles solutions of sodium and potassium hydroxids, but is not nearly so caustic. It is used in the laundry and for cleansing purposes in general.
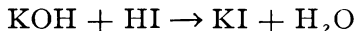
SOME IMPORTANT COMPOUNDS OF THE ALKALI METALS

HALIDS

219. Formation of Halids. The halogens combine directly with the alkali metals to form "halid salts":

$$2 \, Na + Cl_2 \longrightarrow 2 \, NaCl$$
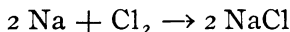
The halogen acids (hydracids) react with the alkalin hydroxids in aqueous solution:

$$KOH + HI \longrightarrow KI + H_2O$$

Other less direct methods of preparation are also employed.

SODIUM CHLORID

220. Salt Making. In this country most of the table salt is obtained from wells bored down into salt beds lying several hundred feet below the surface of the ground. The salt water is pumped up and evaporated in large pans, both by artificial and

the sun's heat. The crystals which at first separate out consist of almost pure salt, and are collected and dried. Sea water in some countries is dammed up at the time of high tide in immense lagoons; the water is allowed to evaporate under the influence of the sun's rays, and the crystals which form are raked out. *Rock salt* is mined in many parts of the globe, and is purified by recrystallization.

221. Properties and Uses. Sodium chlorid forms white cubes which often crystallize in beautiful hopper-like aggregations. Its solubility is but slightly affected by changes of temperature. It is not deliquescent when perfectly pure ; common table salt contains a trace of magnesium chlorid, $MgCl_2$, which is very deliquescent, and causes the salt to stick in the saltcellars or shakers in damp weather. Besides its use as a food and a preservative, salt is used as a glaze for earthenware. Salt is necessary for the preservation of animal life, for the hydrochloric acid contained in the gastric juice of the stomach is derived from it. It is the source from which most sodium compounds are made.

222. Ammonium Chlorid, NH_4Cl. Ammonium chlorid, sometimes called *sal ammoniac*, is obtained by adding hydrochloric acid to the ammonia water obtained in the manufacture of illuminating gas:

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$
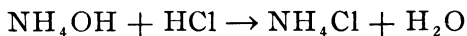
It is a white solid with a sharp, salty taste, and is quite soluble in water. When heated it sublimes, and at a higher temperature dissociates into ammonia and hydrogen chlorid. It is used in electric batteries and to clean metallic surfaces for soldering.

LAWS OF DISSOCIATION; CHEMICAL EQUILIBRIUM.
Suppose a solid A to dissociate into the gases B and C,
and let a, b, and c denote the number of times the
formula weight (§ 140) of each substance is contained
in a liter of the mixture of the three substances. It has
been found by experiment that at the same temperature,
$a/bc =$ a constant. The application of this law thus
expressed algebraically may be illustrated by consider-
ing the dissociation of the white solid, ammonium chlo-
rid. This when heated dissociates into the two gases,
hydrogen chlorid and ammonia. Suppose some ammo-
nium chlorid to be placed in a confined vacuous space
(as a barometric vacuum of one liter's capacity), and
heated to a uniform temperature. A definite amount,
a, of the ammonium chlorid will dissociate into the
amounts b and c of hydrogen chlorid and ammonia,
respectively, and, as above, $a/bc =$ a constant. Sup-
pose now that some ammonia be introduced into the
space and the pressure increased so as to keep the
volume the same. The value of c is thereby increased,
and in order that a/bc may still be equal to a constant,
the other factor in the denominator must decrease.
Hence enough of the ammonia added will combine with
some of the hydrogen chlorid, forming ammonium
chlorid, to restore the equilibrium, and the amount of
ammonium chlorid dissociated is diminished. The same
effect is produced by adding hydrogen chlorid. An
excess of either product of the dissociation diminishes
the amount of the dissociation.

MASS ACTION IN ELECTROLYTES. It is not alone the
nature of reacting substances which determines how
much of a compound can be formed, but also the rela-
tive masses of the reacting substances. Analogous
facts are true of substances undergoing electrolytic
dissociation. To diminish the dissociation of a sub-
stance in solution it is merely necessary to add to the
solution another substance which can yield one or
more of the dissociation products, *viz.*, ions of the first
substance. And an excess of one of the reacting sub-
stances will accomplish the same result in many cases.
Hence the practical rule of adding an excess of the
substance which is to precipitate another substance.

SOLUBILITY PRODUCT. A solution is said to be saturated with a solute at a given temperature when the solute ceases to dissolve. A state of equilibrium then ensues between the solute and the solvent, and if either is changed the equilibrium is disturbed. Thus, a solution of sodium chlorid contains undissociated molecules of NaCl as well as the ions $\overset{+}{\text{N}}$a and $\overset{-}{\text{Cl}}$. The saturated solution contains all the chlorin and sodium ions it can. If hydrogen chlorid, HCl, be passed into such a saturated solution, it dissociates partially into the ions, $\overset{+}{\text{H}}$ and $\overset{-}{\text{Cl}}$. But the solution is already saturated with chlorin ions. Hence some of them are thrown out of solution, and as free sodium ions cannot exist alone in a solution, an equal number of them is precipitated in combination with the chlorin ions, so that solid sodium chlorid appears. The solution keeps saturated with chlorin ions, while the number of sodium ions may be diminished by the addition of hydrogen chlorid. Hydrochloric acid, therefore, is said to precipitate sodium chlorid, or sodium chlorid is less soluble in hydrochloric acid than in pure water.

If m, c, and c' represent numbers of grams of sodium chlorid molecules and of sodium and chlorin ions equal respectively to their molecular or atomic weights and contained in a liter of saturated solution, the equation

$$c \times c' = m \times \text{a constant}$$

has been proved by experiment to be true. Its similarity to the equation found for substances undergoing ordinary dissociation is apparent.

223. Potassium Bromid, KBr, and Iodid, KI. Potassium bromid and iodid are prepared by adding bromin or iodin to a solution of potassium hydroxid until the solution takes on a yellowish tinge. Potassium bromid (iodid) and bromate (iodate) are thus formed:

$$6\,KOH + 6\,Br \rightarrow 5\,KBr + KBrO_3 + 3\,H_2O$$
$$6\,KOH + 6\,I \rightarrow 5\,KI + KIO_3 + 3\,H_2O$$

By heating the potassium bromate (iodate) it is converted into potassium bromid (iodid) and oxygen. Potassium bromid and iodid are white, crystalline solids, soluble in water. They are used in medicine and photography.

224. Ammonium Sulfid, $(NH_4)_2S$. Ammonium sulfid is prepared by passing hydrogen sulfid gas into ammonium hydroxid to saturation, whereby *ammonium hydrosulfid*, NH_4HS, is formed.

$$NH_4OH + H_2S \rightarrow NH_4HS + H_2O$$
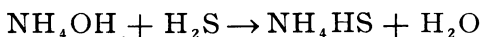
and then adding an equal bulk of the ammonium hydroxid:

$$NH_4HS + NH_4OH \rightarrow (NH_4)_2S + H_2O$$
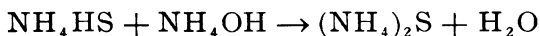
When freshly prepared it is a colorless liquid of disagreeable smell, but on exposure to light turns yellow from separation of sulfur.

SODIUM SULFATE (Glauber's Salt)

225. Preparation. Sodium sulfate, also known as Glauber's salt, occurs in many mineral waters and is formed in the manufacture of nitric acid when sulfuric acid acts upon Chile saltpeter. It is also prepared by the action of sulfuric acid on sodium carbonate, the first step in the manufacture of sodium carbonate by Le Blanc's process (§ 229). Both the acid sulfate, $NaHSO_4$, and the normal sulfate, Na_2SO_4, may be formed in this reaction; the normal salt requires the higher temperature:

$$2NaCl + H_2SO_4 \rightarrow HNaSO_4 + NaCl + HCl$$
$$NaCl + HNaSO_4 \rightarrow Na_2SO_4 + HCl$$
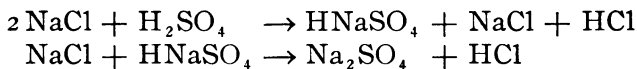
Common salt and concentrated sulfuric acid are

heated in iron or lead pans, and the hydrogen chlorid is absorbed in water. When the formation of the acid salt is completed, it is raked over into a reverberatory furnace (page 114), where, at a higher temperature, it is converted into the normal salt.

226. Properties and Uses. Sodium sulfate combines with ten molecules of water of crystallization, forming a glassy solid, $Na_2SO_4 + 10 H_2O$. It is quite efflorescent, falling away to a white powder when exposed to a dry atmosphere. It is used in glass-making and medicine.

227. Potassium Sulfate, K_2SO_4. Potassium sulfate is found in the salt deposits at Stassfurt. It is a white, crystalline, soluble solid used in making alum and as a fertilizer.

AMMONIUM SULFATE, $(NH_4)_2SO_4$. Ammonium sulfate is made by adding dilute sulfuric acid to ammonium hydroxid, and crystallizing out the white compound formed. It resembles potassium sulfate and is used for similar purposes.

SODIUM CARBONATE, Na_2CO_3 (Washing Soda)

228. Sodium compounds seem to perform the same functions in the economy of marine plants that the corresponding compounds of potassium do in land plants. The ashes of marine plants, or *kelp*, are rich in sodium compounds and were formerly the main source of soda. This compound is now prepared from sodium chlorid or from cryolite.

229. Le Blanc's Process. Sodium sulfate, called "salt cake," is heated in a reverberatory furnace with coal dust and powdered chalk or limestone (calcium carbonate). After the mixture has melted it is raked out to cool, and is then known as "ball

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soda" or "black ash." In the reaction calcium sulfid and carbon monoxid are formed:

$$Na_2SO_4 + CaCO_3 + 4C \rightarrow Na_2CO_3 + 4CO + CaS$$
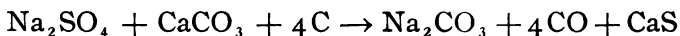
The carbonate of soda is washed out of the black ash, and the solution evaporated to dryness, leaving "soda ash," or crude carbonate of sodium.

230. Solvay's Ammonia-Soda Process. Solvay's ammonia-soda process depends upon the formation of the difficultly soluble acid sodium carbonate, $NaHCO_3$, when an ammoniacal solution of sodium chlorid is saturated with carbon dioxid:

$$NaCl + NH_3 + H_2O + CO_2 \rightarrow NaHCO_3 + NH_4Cl$$
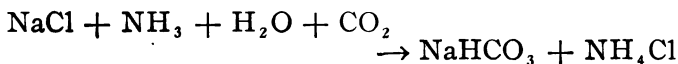
The acid salt is filtered off and converted into the normal salt by heating:

$$2\,NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$
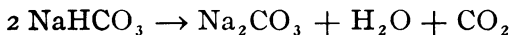
The carbon dioxid thus regenerated is used to precipitate fresh amounts of the acid carbonate. The ammonium chlorid obtained is heated with lime, and the ammonia thus regenerated:

$$2\,NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2\,H_2O + 2\,NH_3$$
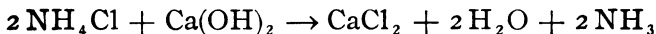
SODIUM CARBONATE FROM CRYOLITE. Cryolite is a double fluorid of sodium and aluminum found principally in Greenland. When heated with quicklime it is converted into insoluble calcium fluorid, CaF_2, and sodium aluminate, Na_3AlO_3:

$$Na_3AlF_6 + 3\,CaO \rightarrow 3\,CaF_2 + Na_3AlO_3$$
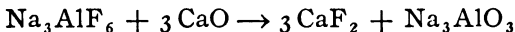
The calcium fluorid is filtered off and the sodium aluminate treated with carbon dioxid, whereby sodium carbonate and insoluble aluminum hydroxid, $Al(OH)_3$, are obtained:

$$2\,Na_3AlO_3 + 3\,H_2O + 3\,CO_2 \rightarrow 3\,Na_2CO_3 + 2\,Al(OH)_3$$
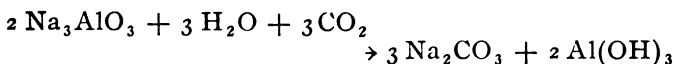
231. Properties and Uses. Sodium carbonate crystallizes with ten molecules of water, forming a glassy, efflorescent solid, commonly called *sal soda* or *washing soda*. It has an alkalin taste and is very soluble. It is extensively used in the laundry and in glass and soap making.

232. Sodium Bicarbonate (*Primary or Acid Sodium Carbonate*), $NaHCO_3$. Sodium carbonate is made by passing carbon dioxid into a solution of sodium carbonate and is a by-product in the ammonia-soda process (§ 230). It, as well as the corresponding potassium compound, $HKCO_3$, is known as *saleratus*. When heated it is converted into the normal carbonates:

$$2\,NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$
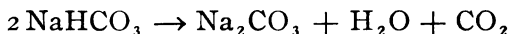
It forms a white powder which is soluble in water.

BAKING POWDERS. Baking powders consist of sodium bicarbonate mixed with some acidifying agent as potassium bitartrate (cream of tartar), $KH(C_4H_4O_6)$, acid calcium phosphate, $CaH_4(PO_4)$, or alum, $K_2Al_2(SO_4)_4$. A "filling" of starch or flour is incorporated so as to prevent any action as long as the powder is kept dry. When water is added to it, the acid liberates the carbon dioxid in the bicarbonate, and when the latter is mixed with dough, the dough is puffed up and becomes filled with little cavities containing carbon dioxid, or, in other words, the dough "rises." The wholesomeness of a baking powder depends not only upon the nature of the solid products, but also upon the care exercised in the selection of pure ingredients and in mixing them in just the right proportions.

233. Potassium Carbonate, K_2CO_3. Potassium carbonate is prepared by leaching wood ashes and evaporating the solution to dryness in iron pots. The residue is called *potash*, and, when calcined,

pearl ash. It is also manufactured from potassium chlorid, KCl, by both the Le Blanc and Solvay processes. It is a white, deliquescent compound, very soluble in water, and is used in the manufacture of soft soap and of glass.

234. Potassium Nitrate, KNO_3. Potassium nitrate, also called *niter* and *saltpeter*, occurs in the juices of many plants and is found in the soil in considerable amounts in certain places in the East Indies. It may be prepared by heaping up animal and vegetable refuse matter with lime, wood ashes, and soil, and keeping the mixture exposed to the air. A microörganism flourishes under such conditions, and slowly brings about the formation of niter, which may be leached out and purified by crystallization. The natural beds of *Chile saltpeter* or *sodium nitrate* were probably formed in somewhat the same manner.

Burning charcoal deflagrates when thrown on niter. Paper soaked in niter solution and dried burns slowly and steadily, and is used for fuses under the name of *touch-paper*. Potassium nitrate has a cooling taste, and is used as a remedy for sore throat under the name, *sal-prunelle*. It is extensively employed in preserving meat and in the manufacture of gunpowder.

GUNPOWDER. Gunpowder is a mixture of about 75 parts of potassium nitrate, 15 of charcoal, and 10 of sulfur. These proportions vary somewhat, each maker having his own formula for each kind of powder. The niter must be free from deliquescent compounds, such as Chile saltpeter, else the powder would become damp. The charcoal is made from light woods so as to catch fire readily, and distilled rather than sublimed sulfur is
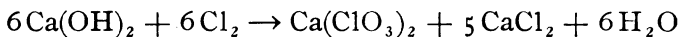
preferable. The three ingredients are first ground and sifted separately, then mixed in the proper proportions and made into a thick paste with water. This paste is subjected to immense pressure and forms what is known as *press-cake*. These cakes are broken up into grains which are sorted according to size in a series of sieves and dried in a steam bath. The grains are polished by placing them in revolving barrels together with a little graphite.

The explosive power of gunpowder is due to the sudden formation of a large volume of gas, mainly carbon dioxid and nitrogen. One volume of the powder gives nearly 4,000 volumes of the gases.
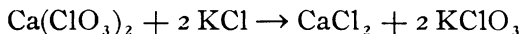
235. Potassium Chlorate, $KClO_3$. Potassium chlorate may be prepared by passing chlorin into a hot, concentrated solution of potassium hydroxid:

$$6\,KOH + 3\,Cl_2 \rightarrow 5\,KCl + KClO_3 + 3\,H_2O$$

It is made more economically by running chlorin into hot milk of lime:

$$6\,Ca(OH)_2 + 6\,Cl_2 \rightarrow Ca(ClO_3)_2 + 5\,CaCl_2 + 6\,H_2O$$

and then having the calcium chlorate formed react with potassium chlorid:

$$Ca(ClO_3)_2 + 2\,KCl \rightarrow CaCl_2 + 2\,KClO_3$$

It is a white, crystalline solid which, mixed with sugar and compressed in tablets, forms the *chlorate of potash tablets* used as a remedy for sore throat. When heated it decomposes into potassium chlorid and oxygen (§ 30). It is employed in the manufacture of matches, fireworks, and smokeless powder.

236. Potassium Cyanid, KCN. Potassium cyanid is formed when nitrogenous substances of animal origin, as hoofs, hides, or wool, are heated with potassium carbonate. It is a white, deliquescent

solid, very soluble in water, and is exceedingly poisonous. It is a good reducing agent, taking oxygen from many compounds to form *potassium cyanate*, KCNO. Silver salts are soluble in its solution, and it is extensively used in the plating of metals by electricity.

RELATIONS BETWEEN THE ATOMIC WEIGHTS OF THE ALKALI METALS. A comparison of the atomic weights of lithium (7), sodium (23), and potassium (39) shows that the sum of the atomic weights of lithium and potassium is just double that of sodium :

$$\frac{7 + 39}{2} = 23$$

Likewise the atomic weight of rubidium (85) is nearly the mean of those of potassium (39) and cæsium (133) :

$$\frac{39 + 133}{2} = 86$$

Exercises

1. Add the atomic weights of chlorin and iodin and divide their sum by two. How does this average compare with the atomic weight of bromin ?

2. How would you distinguish ammonium chlorid from sodium chlorid ?

3. How would you test a washing powder for an ammonium compound ?

4. What are the chief differences between ammonium and ammonia ?

5. How do (*a*) ammonium chlorid and (*b*) ammonium nitrate behave when heated ?

6. How may the existence of potassium compounds in plants be proved ?

7. Why does the electrolysis of an aqueous solution of sodium chlorid give *sodium hydroxid and hydrogen* at the cathode?

8. Which of the following gases would you dry with *solid* caustic potash : Ammonia, carbon monoxid, carbon dioxid, oxygen?

Problems

1. What is the percentage of potassium in (*a*) potassium bromid, KBr, (*b*) potassium nitrate, KNO_3 ?

2. 10 $g.$ of gunpowder, when exploded, yielded 3 $l.$ of gas measured at 0° and 760 $mm.$ What would be the volume at 1,800°, and what would be the pressure exerted if the volume was kept unchanged ?

3. Diehl, in 1862, obtained from 15.5533 $g.$ of lithium carbonate, Li_2CO_3, by dissolving it in sulfuric acid, 9.2414 $g.$ of carbon dioxid. Calculate the atomic weight of lithium on the basis that the atomic weights of carbon and oxygen are 12.0 and 16.0, respectively.

4. Dumas, in 1859, by adding silver nitrate to a solution containing 28.7875 $g.$ of sodium chlorid, obtained a precipitate of silver chlorid containing 53.1375 $g.$ of silver. What is the atomic weight of sodium, if the atomic weights of silver and chlorin are 107.94 and 35.45, respectively ?

5. Penny, in 1839, changed 404.186 $g.$ of sodium chlorate, $NaClO_3$, into 222.016 $g.$ of sodium chlorid by heating the chlorate with hydrochloric acid. The atomic weights of chlorin and of oxygen are 35.45 and 16.00 ; what is the atomic weight of sodium?

6. How much potassium is required to decompose enough water to yield 226 $l.$ of hydrogen at 20° and 742 $mm.$?

7. What is the percentage of water crystallization in Glauber's salt, $Na_2SO_4 + 10 H_2O$, and how does its volume in the free state compare with its volume when combined with the salt, if 100 $g.$ of Na_2SO_4 occupy 37.7 $c.c.$ and 100 $g.$ of $Na_2SO_4 + 10 H_2O$, 69.5 $c.c.$?

EQUIVALENTS; MOLECULAR AND ATOMIC WEIGHTS

237. Equivalent Weights. The alkali metals, sodium and potassium, decompose water with evolution of hydrogen, and it has been found that 23^g· of sodium and 39^g· of potassium are required to separate out from the water 1^g· of hydrogen. Certain other metals, such as magnesium, iron, zinc, and aluminum, dissolve in acids with evolution of hydrogen; 1^g· of hydrogen is liberated by 12^g· of magnesium, 28^g· of iron, 32.5^g· of zinc, or 9^g· of aluminum. The weights of metals required to displace the unit weight of hydrogen are definite and are called the *equivalent weights.*

Although but relatively few elements displace hydrogen from water or acids, the conception of equivalent weights may yet be applied to all the elements. Thus, the analysis of water proves it to contain 8 parts by weight of oxygen and 1 part of hydrogen. The equivalent weight of oxygen is therefore 8. Now oxygen combines with most other elements so that the analysis of their oxids will permit us to determine their equivalent weights. Thus, magnesium oxid contains 12 parts of magnesium and 8 parts of oxygen. Hence the equivalent weight of magnesium is 12. Similarly, 23^g· of sodium, 32.5^g· of zinc, and 28^g· of iron each unite with 8^g· of oxygen, and the equivalents found by direct comparison with hydrogen are confirmed.

Zinc, magnesium, and some other metals, when placed in a solution of copper sulfate, dissolve, while the copper separates out in the metallic form. The ratio of the weight of the metal dissolved to that of the copper precipitated is that of their equivalents. Silver neither displaces hydrogen nor combines readily with oxygen, but its equivalent can be found by precipitating it from solution by means of zinc or some other metal. It is possible in the case of every element to find some other element with which it may react in such a way that its equivalent may be determined.

To determine the equivalent of an element, then, it is necessary to find by experiment what weight of the element combines with 1 $g.$ of hydrogen or takes the place of 1 $g.$ of hydrogen in a compound. If this is impracticable, we must ascertain the weight of it, which combines with or takes the place of 8 $g.$ (more exactly, 7.94 $g.$) of oxygen, or the equivalent weight of any other element.

238. System of Equivalents. A number may thus be found which represents a definite weight of each element and which is chemically equivalent to the unit weight of hydrogen. The system of equivalents is based on experiment alone, and would be very simple and convenient if it were not for the fact that certain elements have more than one equivalent. For example, copper forms two oxids, one red and the other black. From an analysis of the black oxid the equivalent of copper is 31.5, while from an analysis of the red oxid, its equivalent is just twice 31.5 or 63. Now there is no way of deciding on experimental evidence alone

which equivalent of an element is to be adopted, and a system of combining numbers based on equivalents alone would be quite arbitrary and would give rise (as it actually did) to endless controversy as to which equivalents should be chosen.

239. Electro-chemical Equivalents. If the same current of electricity be sent through a solution of a silver, a zinc, or an iron salt and any number of acids, the continued ratio of the weights of silver, zinc, or iron, and hydrogen thrown out of solution will be $108 : 32.5 : 28 : 1$; that is, the ratio will be that of the chemical equivalents of the elements. Faraday discovered this fact and deduced therefrom the law:

Equal electric currents liberate in equal intervals of time quantities of elements proportional to their chemical equivalents.

Just as certain elements have two or more chemical equivalents, so do they have two or more electro-chemical equivalents. Also, some elements do not form solutions conducting electricity, so that their electro-chemical equivalents cannot be determined directly.

240. Equivalent Weights of Compounds. The equivalent of any acid is that weight of it which combines with one equivalent of a univalent metal; the acid contains at least one equivalent of hydrogen replaceable by a univalent metal. Thus, the equivalent weight of nitric acid, HNO_3, is 63, and is the same as its formula weight; that of sulfuric acid, H_2SO_4, however, is 49, which is one-half its formula weight. The equivalent of any base is that weight of it which neutralizes one equivalent of an

acid. Thus, 40$^{g.}$ of sodium hydroxid, NaOH, neutralizes 63$^{g.}$ of nitric acid; hence the equivalent weight of sodium hydroxid is 40, which is also its formula weight. The equivalent weight of the salt, silver nitrate, $AgNO_3$, is the same as that of its formula weight, *viz.*, 170, because that weight exactly reacts with one equivalent of hydrochloric acid, HCl.

In similar fashion the equivalent weights of all compounds can be fixed. Each case has to be considered by itself. Attention will be called to the matter in studying the various substances in the sequel.

241. Law of Equivalent Proportions. The relationships just set forth are entirely general and true of all substances. They have led to the establishment of the Law of Equivalent or Reciprocal Proportions:

The weights of different substances combining with a fixed weight of a given substance are either the same as, or stand in a simple integral relation to, the weights of these substances which combine with one another.

HISTORICAL NOTE. The first notions of the facts covered by this law were gained towards the end of the eighteenth century, but the full import of the law was not recognized until chemists, chief among whom was Berzelius, began to fix these equivalents with accuracy. The system of equivalents which arose through their labors involved too many inconsistencies, however, and it was not until Avogadro's Hypothesis was revived by Cannizzaro in 1858 and the Doctrine of Valence was propounded that order was introduced.

242. Avogadro's Hypothesis. The simple relationships between the volumes of combining gases discovered by Gay-Lussac in 1808 and expressed

as the Law of Volumetric Proportions (§ 51) led
Avogadro in 1811 and Ampere in 1814 to the follow-
ing hypothesis:

*Equal volumes of all gases, at the same temperature
and pressure, contain equal numbers of molecules.*

The value of this hypothesis was not recognized
until 1858, when Cannizzaro showed what an excel-
lent basis it afforded for the fixing of molecular
weights. It is to be carefully noted that Avogadro's
hypothesis refers only to molecules and not to
atoms.

**243. Determination of Molecular Weights by
Means of Avogadro's Hypothesis.** It is an experi-
mental fact that two volumes of hydrogen combine
with one volume of oxygen to produce two volumes
of steam. It is also an experimental fact that one
liter of hydrogen or oxygen weighs twice as much
as does the smallest amount of these gases con-
tained in a liter of any of their gaseous compounds;
hence the formulas of hydrogen and of oxygen in
the free state are H_2 and O_2, respectively.

In terms of the Atomic Theory we say that a
molecule of hydrogen and oxygen is made up of
two atoms, and that their atomic weights are half
their molecular weights. The equation represent-
ing the formation of water from its elements is:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$
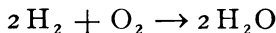
Suppose now that a certain volume of oxygen
contains a billion molecules. Then, by Avogadro's
Hypothesis, an equal volume of any other gas, at
the same temperature and pressure, must contain
the same number of molecules. The equation may
then be read:

Two billion molecules of hydrogen unite with one billion molecules of oxygen to form two billion molecules of water.

Dividing both members of the equation by a billion, we have:

Two molecules of hydrogen unite with one molecule of oxygen to produce two molecules of water.

But the weights of equal volumes of oxygen and hydrogen are to each other as 32 : 2. Hence the weights of their molecules must be in the same ratio. One liter of water vapor weighs 0.805 $^{g.}$ and one liter of hydrogen 0.09 $^{g.}$ Hence steam weighs $\dfrac{0.805}{0.09} = 9$ (nearly) times as much as the same volume of hydrogen, *i. e.*, its specific gravity is 9. The weight of a steam molecule is therefore 9 times that of a hydrogen molecule, or $9 \times 2 = 18$ times that of a hydrogen atom. Since the specific gravity of steam referred to hydrogen is 9, its molecular weight is equal to twice its specific gravity.

If then we adopt Avogadro's Hypothesis, we are in a position to find molecular weights by means of vapor density determinations. By the molecular weight of a gas we understand the number of times heavier its molecule is than the weight of one atom of hydrogen. Now the weight of *one atom* of hydrogen is the standard in the determinations of molecular weights, while the weight of *one molecule* of hydrogen (equal to the weight of *two atoms*) is taken as the standard in density determinations. Hence:

To find the molecular weight of a gas, double its density referred to hydrogen, or divide the weight of a liter of it by 0.045, the elemental weight of hydrogen.

244. Determination of Atomic Weights by Means of Avogadro's Hypothesis. While it is thus a comparatively simple matter to fix the molecular weight of a vaporizable substance by Avogadro's Hypothesis, atomic weights can be found only when the number of atoms in a molecule of an element is known. All the gaseous compounds containing the element must be analyzed and their molecular weights found by vapor density determinations. The results are compared and the smallest amount of the element contained in a molecule of any of its gaseous compounds chosen as its atomic weight. Thus, of the almost innumerable compounds of carbon which have been investigated, not one has been found to contain in its molecule a relative weight of less than 12 for carbon. Hence, 12 is taken as the atomic weight of carbon.

In this way the conclusion has been reached that most elements have molecular weights which are multiples of their atomic weights. The molecule of hydrogen, nitrogen, and oxygen we have found to consist of two atoms each, and several other elementary gases have a similar structure. Certain other elements, such as phosphorus and sulfur, have gaseous molecules that are made up of more than two molecules, while still others, such as mercury and zinc, have molecules which are identical with their atoms.

Molecular weights as determined by means of Avogadro's Hypothesis apply to gaseous substances only, and may be different when the substances are in the liquid or the solid state. The special methods which have been devised to ascertain the molecular

weights of liquids and solids are too difficult to be discussed here. From lack of more definite knowledge it is assumed that the solid and liquid molecules contain the same number of atoms as they do when vaporized.

245. How to Find the Atomic Weight of Nitrogen. We know by experiment the vapor density and the composition of a number of compounds of nitrogen, and can deduce therefrom their molecular weights, the proportion of the elements in each compound and its formula. In the following table are given the mass and volume relationships of a number of nitrogen compounds.

NAME	*Vapor density*	*Molecular weight*	*Weight of nitrogen*	*Weight of other elements*	*Formula*
Ammonia	8.5	17	14	3	NH_3
Hydrazin	16	32	2×14	4	N_2H_4
Hydrazoic acid	22.5	43	3×14	1	N_3H
Cyanogen	26	52	2×14	24	C_2N_2
Nitrogen monoxid	22	44	2×14	16	N_2O
Nitrogen dioxid	15	30	14	16	NO

In looking down the column, "Weight of nitrogen," we see that 14 is the smallest weight that occurs, and hence conclude that 14 is the atomic weight of nitrogen. If, however, in the future some other compound of nitrogen should be discovered in which the weight of hydrogen was found to be less than 14, the lesser number would have to be taken as the atomic weight of nitrogen. It is apparent that we can never be quite sure that we know the right atomic weight of an element, for compounds may yet be discovered in which the atomic weight is different from that now adopted.

246. Equivalent and Atomic Weights Compared.

In the following table are given the equivalent and atomic weights of some familiar elements; their valencies are marked by accents.

ELEMENT	Equivalent weight	Atomic weight	Atomic weight / Equivalent weight
Aluminum'''____ _____	9	27.1	3 (nearly)
Chlorin' ___ __ _____	35.43	35.43	1
Copper' or '' ____ _____	63.6 or 31.8	63.6	1 or 2
Iron''_____ _____	28	56	2
Magnesium''_____	12.2	24.4	2
Oxygen''___ __ . _____	8	16	2
Lead''___ _____	103.46	206.92	2
Potassium'_____	39.1	39.1	1
Sodium'_ _____	23	23	1
Tin'' or ''''_____ _____	29.8 or 59.5	119	2 or 4
Zinc''_____	32.7	65.4	2

This table might be extended to cover all the elements, but enough examples are given to illustrate the relationships. There has always been a certain arbitrariness exercised in the fixing of equivalents; those given are such as may be determined by the student himself. It is seen that the atomic weights are never less than the equivalent weights and may be one, two, three, or four times as large. It may not be amiss to reiterate that the numbers representing the equivalents denote how many times heavier the element is than the weight of hydrogen to which it is equivalent, while the numbers standing for the atomic weights show how much heavier the atom of the element is than the atom of hydrogen.

247. Equivalents and Valence.

Reference to the table just given shows that chlorin, sodium, and potassium are univalent and their equivalent and

DUMAS

GRAHAM

STAS

HOFMANN

Plate 7

THOMAS GRAHAM

1805-1869; English

Discovered laws of diffusion of gases, basicity of acids. Contributed to the knowledge of water of crystallization and of dialysis

JEAN BAPTISTE ANDRÉ DUMAS

1800-1884; French

Fixed many atomic weights. Ascertained with great accuracy the composition of water and air. Devised method of finding vapor densities

AUGUST WILHELM HOFMANN

1818-1892; German

Active in domain of organic chemistry. Discovered important coal-tar dyes

JEAN SERVAIS STAS

1813-1891; Belgian

Made accurate determinations of the atomic weights of many elements

Plate V

atomic weights are the same. Iron, magnesium, oxygen, lead, and zinc are usually bivalent, and their equivalents are half their atomic weights. Aluminum is trivalent, and its equivalent is one-third its atomic weight. *Univalent* copper has its equivalent and atomic weight equal, while *bivalent* copper has an atomic weight twice that of its equivalent. *Bivalent* or *quadrivalent* tin has an equivalent either one-fourth or one-half the atomic weight. By comparing all the elements in this way we find that:

The atomic weight of an element is equal to its equivalent multiplied by its valency.

We now can see how the system of molecular and atomic weights supplanted that of equivalents. All elements were at first supposed to have the same combining power; they were *equal-valued* or *equivalent*. When Avogadro's Hypothesis was adopted, however, it became evident that they were not equal-valued, but that some had a greater combining power than others. From this conception arose the Doctrine of Valence. The system of equivalents was based on mass-relationships. With Avogadro's Hypothesis came the requirement that volume-relationships should also be considered, and that the choice of molecular weights is regulated by a physical property, that of vapor density.

248. Equivalents and Valence of Radicals. Radicals as well as elements have equivalents and valence. In nitric acid, HNO_3, the radical, NO_3, is combined with one atom of hydrogen, and it is therefore univalent. The radical, SO_4, combines with two atoms of hydrogen to form sulfuric acid, H_2SO_4, and is therefore bivalent.

15

249. Basicity and Acidity. When the formula weight and the equivalent weight of an acid are the same, the molecule of the acid contains but one hydrogen atom which is replaceable by a univalent metallic atom or radical to form a salt. Such an acid is said to be *monobasic*. Thus nitric acid, HNO_3, is monobasic, and forms salts of the type $M'NO_3$, where M' represents any univalent metal or metal-like radical. Potassium nitrate, $K'NO_3$, and ammonium nitrate, $(NH_4)'NO_3$, are examples. Hydrochloric acid, HCl, and acetic acid, $H(C_2H_3O_2)$, are also monobasic, and there are many others.

When the formula weight of an acid is twice its equivalent weight, the molecule of the acid contains two hydrogen atoms which are replaceable by two univalent metallic atoms or radicals or by one bivalent metallic atom or radical. Thus, sulfuric acid has a formula weight of $98^{g.}$ and an equivalent weight of $49^{g.}$ and forms salts of the type $M'SO_4$, where M' is univalent, or $M''SO_4$, where M'' is bivalent. Sodium sulfate, Na_2SO_4, and calcium sulfate, $Ca''SO_4$, are examples.

Likewise, the molecules of *tribasic* acids contain three hydrogen atoms replaceable by (*a*) three univalent metallic atoms or radicals, (*b*) one univalent and one bivalent metallic atom or radical, and (*c*) one trivalent atom or radical. Their formula weight is three times their equivalent weight. Thus, phosphoric acid, H_3PO_4, yields the salts, tri-potassium phosphate, K_3PO_4, aluminum phosphate, $AlPO_4$; but no salt of the type $M''M'PO_4$ has been prepared.

When the equivalent and formula weights of a base are the same, the molecule of the base contains

one hydroxyl group replaceable by the univalent anion of an acid. Thus, the hydroxids of sodium and potassium, NaOH and KOH, form salts of the type NaA′ and KA′, where A′ is a univalent anion. Such bases are said to be *monacidic*.

Likewise, there are *diacidic* bases, such as calcium hydroxid, $Ca(OH)_2$, and boron hydroxid, and triacidic bases, such as bismuth hydroxid, $Bi(OH)_3$, but bases with an *acidity* greater than three are not known to exist.

250. Acid and Basic Salts. Dibasic acids may form two series of salts. In one but half of the hydrogen is replaced by a univalent metal or radical, while in the others all of the hydrogen is replaced. Thus, sulfuric acid forms the series of salts of the type $M′HSO_4$, where M′ is a univalent metal or radical, and also the series $M_2′SO_4$. An example of the first series is hydrogen sulfate (also called acid sodium sulfate), $NaHSO_4$; an example of the second series is disodium sulfate or normal sodium sulfate (usually called, simply, sodium sulfate), Na_2SO_4.

Tribasic acids in like manner may form three series of salts, since their hydrogen is replaceable in three stages.

Salts of di- and tribasic acids still containing replaceable hydrogen are called *acid salts*. They may usually be converted into normal salts when enough of the base is added to replace the hydrogen. Conversely, normal salts are converted into acid salts by treatment with more of the acid.

Usually solutions of acid salts have an acid reaction, but if they are composed of a strong base and

a weak acid, the reaction may be alkalin, as is the case with disodium hydrogen phosphate, Na_2HPO_4, and sodium hydrogen carbonate (ordinarily known as bicarbonate of soda), $NaHCO_3$.

In like fashion the hydroxyl groups of bases containing a bivalent or trivalent metal might be substituted in two or three stages. This does not take place in the case of the common bases, however; that of bismuth is about the only one we shall encounter.

Problems

1. A certain gas is 22 times heavier than an equal volume of hydrogen. What is its molecular weight? What familiar gas has that molecular weight?

2. If 50 *c.c.* of methane contain 10^{20} molecules, how many molecules will 100 *c.c.* of acetylene contain, if the conditions of temperature and pressure are the same for both gases?

3. A piece of lithium was placed on water; it dissolved, forming lithium hydroxid, LiOH, and evolved 656 *c.c.* of hydrogen at 21° and 743 *mm.*. If the equivalent of this metal is 7, what was the weight of the lithium taken?

4. The weight of a liter of ether vapor at 100° and 760 *mm.* is 2.44 *g.*. What is its molecular weight?

5. Lime, CaO, contains 71.43 per cent of calcium and 28.57 per cent of oxygen. What is the atomic weight of calcium?

6. The molecular weight of bromin is 160. What is its vapor density referred to hydrogen?

7. If a liter of sulfur dioxid weighs 2.86 *g.*, what is its molecular weight?

8. How many cubic centimeters of carbon monoxid weigh 1.88 *g.*?

9. The vapor density of chlorin is 35.45; what is its molecular weight?

10. 3.808 *g.* of a gas occupies 2703.4 *c.c.* at 15° and 740 *mm.*. Find its molecular weight.

11. The specific gravity of mercuric chlorid referred to air is 9.8. It contains 73.93 per cent of mercury (Hg) and 26.07 per cent of chlorin (Cl). What then is the formula for mercuric chlorid?

12. Calculate the formulas of the compounds having the following percentage composition and vapor density :

(a) C = 92.3% ; H = 7.7% ;   vapor density = 39
(b) C = 73.8% ; H = 8.7% ; N = 17.5% ; vapor density = 80.2
(c) C = 39.9% ; H = 6.7% ; O = 53.4% ; vapor density = 30.5
(d) C = 10.04% ; H = 0.84% ; Cl = 89.12% ; vapor density = 59.7

13. If (as was the case in the second quarter of the nineteenth century) the unit of comparison were O = 100, what would be the equivalents of (a) sodium, (b) hydrogen, (c) magnesium ?

14. Gladstone and Hibbert, on passing the same electric current through solutions of zinc and silver solutions, obtained quantities of the metals in the ratio of 1 (Zn) : 3.298 (Ag). If the equivalent of silver is 107.94, what is that of zinc ?

15. What is the equivalent of nickel if it dissolves in acids with the evolution of a mass of hydrogen equal to 3.411 per cent of its own mass ? What is its atomic weight if it is bivalent ?

16. If the atomic weight of silver is 107.94 and if the same electric current, on passing through solutions of silver and copper salts, precipitates weights of the metals in the ratio of 1 (Cu) : 3.408 (Ag), what is the atomic weight of copper ?

17. If copper oxid, heated in an atmosphere of hydrogen, lost 59.7893g. of oxygen and formed 67.2825g. of water, what is the atomic weight of (a) oxygen referred to hydrogen as one, and (b) hydrogen referred to oxygen as sixteen ?

18. If 750 c.c. of carbon monoxid weigh 0.94g., what is the molecular weight of the compound ?

19. 45.731g. of silver combine with chlorin to form 60.7496 g. of silver chlorid, AgCl. If the equivalent of chlorin is 35.45, what is that of silver ?

20. If a certain current of electricity deposited 31.7g. of copper, how much (a) silver, (b) zinc would it deposit ?

CHAPTER XX

METHODS OF DETERMINING MOLECU-
LAR AND ATOMIC WEIGHTS

251. Vapor Density. When a chemist has pre-
pared a substance which, from its method of prepara-
tion and its properties, he has reason to believe has
never been obtained before, he analyzes it to find
out the proportions in which its constituent ele-
ments are combined. From the percentage compo-
sition (§ 138) he can deduce a formula, which, how-
ever, is still doubtful (§ 139) unless he has some
means of finding the weight of a liter of the sub-
stance in gaseous (or dissolved, cf. below) form.
From the weight of a liter of the vapor he can
readily find its specific gravity with reference to
hydrogen, and double its vapor density gives, by
Avogadro's Rule (page 204), its molecular weight.
Vapor density determinations are then indispen-
sable in the fixing of molecular weights.

The methods of determining the weights of
definite volumes of gases belong more to physics
than to chemistry. Certain methods of finding
vapor densities, however, are so frequently used in
chemistry that they deserve attention here.

DUMAS' METHOD. The neck of a round-bottomed
flask is drawn out to a fine point. The flask is then
weighed and warmed a little, with its point dipping
into the liquid (say alcohol) whose vapor density is to
be found. As the air expanded by the warming cools

and contracts, some alcohol is drawn into the flask.
The flask is now placed in a vessel (Fig. 33) containing
water or oil, the temperature of which is raised some-
what above the boiling point of alcohol.   The alcohol
vaporizes and drives the air
from the flask until finally
the vapor fills the flask at
the temperature of the bath
and the barometric pressure.
The tip of the flask is then
sealed by melting it in a
blowpipe flame, and the flask
removed and weighed.   The
tip is broken off under a
liquid such as water or mer-
cury, and the volume of the
flask found by measuring the
amount of the liquid which
enters the flask.

    An example will make
the calculations clear:
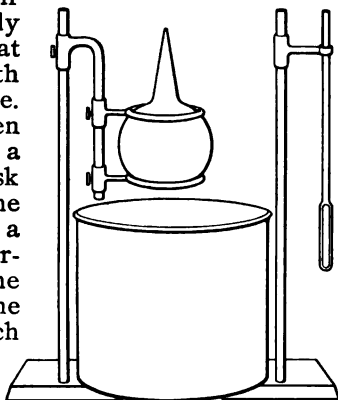
Fig. 33 — APPARATUS FOR DETERMINING
THE VAPOR DENSITY OF A LIQUID BY
DUMAS' METHOD

    Liebig, in 1835, found
that a flask containing
289.5 $^{c.c.}$ of dry air at 12.8° and 751 $^{mm.}$ weighed 48.332 $^{g.}$.
When filled with the vapor of aldehyde at 53.5° and
751 $^{mm.}$ it weighed 48.471 $^{g.}$.   What is the vapor density
of aldehyde?

    Solution: The real weight of the flask filled with aldehyde
vapor is equal to its apparent weight (48.471 $^{g.}$) increased by the
weight of the air it would contain at 12.8° and 751 $^{mm.}$. To find
what this weight would be, it is necessary to calculate the volume
at 0° and 760 $^{mm.}$ which 289.5 $^{c.c.}$ of dry air at 12.8° and 751 $^{mm.}$
would occupy. This volume on calculation comes out 273.1 $^{c.c.}$.
Now as, under standard conditions, 1 $^{c.c.}$ of dry air weighs 0.00129 $^{g.}$
the 273.1 $^{c.c.}$ weigh 0.3523 $^{g.}$. Adding this to the apparent weight
(48.471 $^{g.}$) we find the true weight of the flask filled with aldehyde
vapor to be 48.8233 $^{g.}$. Subtracting the weight of the flask from
this gives 0.4913 $^{g.}$ as the weight of the aldehyde vapor.

    This weight occupies at 53.5° and 751 $^{mm.}$ a volume of 289.5 $^{c.c.}$,
which when reduced to standard conditions becomes 239.3 $^{c.c.}$;
239.3 $^{c.c.}$ of aldehyde vapor weighing 0.4913 $^{g.}$, 1 $^{c.c.}$ would weigh

0.4913/ 239.3 = 0.002053 ; and as 1 $^{c.c.}$ of hydrogen under normal conditions weighs 0.00009$^{g.}$, the vapor density of aldehyde is 0.002053 /0.00009 = 22.8.

VICTOR MEYER'S METHOD. The apparatus (Fig. 34) consists of a "jacketing tube," B, the lower end of which is somewhat enlarged. In this jacketing tube is suspended the tube CA, which has a delivery tube at D, the mouth of which is placed under a graduated tube E filled with water and inverted in the pneumatic trough F. Suppose the vapor density of chloroform is to be determined. A few drops are weighed out on a delicate balance to tenths of milligrams in a tiny glass-stoppered bottle. Water is boiled in B, the rapidity of the boiling being so regulated that the steam is condensed before it reaches the mouth of B. In this way the tube CA is heated throughout its wider portion to nearly 100°. The stopper of the bottle is loosened a little and then bottle and stopper are dropped into the tube CA, which is immediately closed with a rubber stopper. As chloroform boils at 62°, it is rapidly converted into a vapor which forces out the stopper of the bottle, and then lifts up the air in the tube, which is thereby pushed over into the graduated tube. The volume of this air at the temperature and pressure of the room is equal to the volume that the chloroform vapor would occupy if it could be cooled to the same temperature without condensation. When the weight and the volume of the chloroform vapor have thus been determined, its density is calculated in a way similar to the following :

Fig. 34
APPARATUS
FOR DETER-
MINING THE
VAPOR DEN-
SITY OF A
LIQUID BY VIC-
TOR MEYER'S
METHOD

V. Meyer and C. Meyer, in 1878, determined the vapor density of iodin, using in the jacketing tube a liquid whose boiling point is 261°. 0.1157$^{g.}$ of iodin were taken and the volume of the air displaced was 11.6$^{c.c.}$ at 16.1° and 722.3$^{mm.}$. Find the vapor density of iodin.

Solution: As the air was collected over water, its vapor tension (13.6 *mm.* at 16°, cf. § 28) must be subtracted from the barometric pressure. The 11.6 *c.c.* of air reduced to standard and dry conditions would then occupy 10.22 *c.c.*, which would also be the volume of 0.1157 *g.* of iodin, if it could remain gaseous at 0° and 760 *mm.*. One cubic centimeter of iodin would then weigh 0.1157 /10.22 = 0.01132 *g.*, and as one cubic centimeter of hydrogen under normal conditions weighs 0.00009 *g.*, the vapor density of iodin is 0.01132 /0.00009 = 125.8.

252. Other Methods of Determining Molecular Weights.

Many substances are so involatile or so readily decomposed at elevated temperatures that their vapor densities cannot be determined. Of the other methods that have been devised, those that have to do with substances in a state of solution have received a wide application.

253. Analogy Between the Gaseous and the Dissolved States.

The condition of a substance in solution resembles in many particulars its condition when vaporized. In both states the molecules are comparatively far apart. Just as a gas spreads out and occupies any volume allowed it, so does a dissolved substance spread out and occupy the volume of the solvent. A liquid placed in a vacuum vaporizes and the amount of vapor formed depends mainly upon the temperature. A solid dissolves when placed in a suitable liquid and the amount dissolved also depends to a certain extent upon the temperature. These and many other analogies led van't Hoff in 1886 to apply the Gas Laws and Avogadro's Hypothesis to solutions.

254. Osmotic Pressure.

The analogy between the gaseous and dissolved states is so close that we should expect to find in solutions something analogous to one of the most characteristic features

of gases, *viz.*, that of pressure. And indeed it may be shown that dissolved substances exert a pressure quite analogous to that of gases. All that is needed to bring into evidence this *osmotic pressure* is to separate a solvent from its solution by a sieve-like partition or *semi-permeable membrane*, which will permit the molecules of the solvent to pass through, but will prevent the passage of the dissolved molecules. The dissolved molecules press against this membrane, and if any device for measuring pressure be connected with the solution, its amount may be measured. The result of the action of this pressure is that the volume of the solution increases, since more and more molecules of the solvent pass through the partition to occupy the space between the mutually repellent molecules of the dissolved substance. The direct measurement of osmotic pressures is difficult, as suitable semi-permeable membranes are not easy to prepare. It has been proved, however, that the lowering of the freezing point or the raising of the boiling point of a liquid brought about by the solution of another substance is directly proportional to the osmotic pressure. Hence, freezing and boiling point determinations enable us to ascertain indirectly osmotic pressures.

255. Depression of the Freezing Point of Solutions. A method of ascertaining the molecular weights of dissolved substances had been worked out by Raoult in 1882, some time before van't Hoff had put forth his Theory of Solutions. It depends upon the lowering of the freezing point of a solution due to the addition of some soluble substance. Raoult found that:

When in equal amounts of the same solvent, equal weights of different substances are dissolved, the depressions of the freezing point vary inversely as the molecular weights of the dissolved substances.

If m and m' are the molecular weights of two substances, and l and l' are the corresponding depressions of the freezing point produced by the solutions of equal weights of the substances in the same amounts of the solvent, then:

$$m : m' : : l' : l$$

Whence,

$$m = \frac{m'\, l'}{l}$$

To start with, it is necessary that the molecular weight of one substance in solution be known. This has to be found by a vapor density determination. The depression of the freezing point brought about by dissolving one gram of this substance in 100^g. of the solvent is determined once for all, and this represents the product $m'\, l'$, which thus has a constant value. One gram of a substance of unknown molecular weight is then dissolved in 100^g. of the same solvent, and the lowering of the freezing point determined. From these data the unknown molecular weight may be calculated by means of the above formula.

256. Elevation of Boiling Points. A law very similar to that for the depression of the freezing point was also established by Raoult with reference to the raising of the boiling point of a liquid by solution of a substance. If b and b', representing the boiling points of solutions of the same strength of different substances in the same solvent, be

substituted for l and l' in the previous paragraph, the expression:

$$m = \frac{m'\,b'}{b}$$

is the algebraic statement of the law in question. The elevation of the boiling point occasioned by dissolving one gram of a substance of known molecular weight in 100$^g\cdot$ of the solvent is found, from which the value of the constant $m'\,b'$ is calculated. One gram of a substance of unknown molecular weight is dissolved in 100$^g\cdot$ of the solvent, and from the rise in boiling point the molecular weight is computed.

257. Specific Heat. Different amounts of heat are required to warm equal weights of different substances through the same temperature interval, and the ratio of the amount of heat required to warm a given (unit) weight of a substance through one degree to the amount of heat required to warm an equal weight of water through one degree is called the *specific heat* of that substance. Inasmuch as water has the greatest capacity for absorbing heat, of all known definite chemical substances, specific heats are less than unity and are usually expressed as decimal fractions.

258. Dulong and Petit's Law. In 1819 two French chemists, Dulong and Petit, determined the specific heats of a number of elements, and found that the products of the atomic weights and the specific heats of the elements were approximately the same. This product is termed the *atomic heat*, and the Law may be stated as follows:

The atomic heats of all the elements are the same.

A few data will serve to illustrate this law :

ELEMENT	Specific Heat	Atomic Weight	Atomic Heat
Mercury _____ ____	0.032	200	6.4
Zinc _____ _____	0.098	65.4	6.5
Silver_____	0.059	107.9	6.4
Gold_____	0 033	197.2	6 5

The Law may also be put in this way :

The specific heats of elements are inversely proportional to their atomic weights.

259. Determination of Atomic Weights with the Aid of Dulong and Petit's Law. To apply Dulong and Petit's Law we have merely to divide the constant number, 6.4, by the specific heat of the element in question, and the quotient is approximately the atomic weight sought. Thus, suppose we have found the specific heat of lead to be 0.031. Dividing 6.4 by 0.031 we get 206.5 as the required atomic weight. While results by this method are not very exact, they yet serve to distinguish between two questionable atomic weights for the same element. Thus, lead forms several oxids, the analysis of which shows that the atomic weight of lead may be either 206 or 103. Of these the specific heat shows that 206 is to be chosen.

METHODS BUT APPROXIMATE. The foregoing methods are all at best mere approximations; they simply furnish a means of deciding between a molecular weight and some multiple of it. The accurate values are found only by means of quantitative analyses. Thus, the formula of silver chlorid is AgCl or some multiple of AgCl, as Ag_2Cl_2 or Ag_3Cl_3. The molecular weight of AgCl is 143.28. The vapor density of silver chlorid has been found to be 82, from which, by Avogadro's Hypothesis,

a molecular weight of 164 is obtained. Now although 143.28 and 164 are by no means equal, yet they are more nearly equal than are 164 and 2×143.28 ($= 287.56$), so that there is no doubt but that the formula AgCl is best in accordance with the hypothesis.

Problems

1. Dumas and Peligot, in 1835, found that a flask of 484 *c.c.* capacity weighed at 21° and 760 *mm.* lost 0.069 *g.* when filled with the vapor of wood alcohol at 100°. Find the vapor density of wood alcohol.

2. V. Meyer and H. Biltz, in 1889, found that when 0.0589 *g.* of silver chlorid was vaporized at 1736° it displaced 8.6 *c.c.* of nitrogen (with which the apparatus was filled), at a temperature of 13.40, and a pressure of 752.7, the nitrogen being collected over water. What is the vapor density of silver chlorid?

3. 0.1561 *g.* of a compound in a Victor Meyer's vapor-density apparatus expelled 32.1 *c.c.* of dry air at 20° and 744 *mm.*. What is (*a*) its vapor density, (*b*) its molecular weight?

4. What is the formula of mercuric chlorid as deduced from the following data? Weight of flask full of vapor at 350° and 758.4 *mm.* = 27.401 *g.*. Capacity of globe = 250 *c.c.*.

5. Determine the vapor density of phosphorus trichlorid from the following data: Weight of flask full of vapor at 100° and 761 *mm.* = 40.773 *g.*. Capacity of globe = 280 *c.c.*.

6. What is the vapor density of ether as calculated from the following data: Weight of flask full of air at 19° and 741.5 *mm.* = 49.632 *g.*. Weight of flask full of vapor at 82.5° and 740.3 *mm.* = 49.995 *g.*. Weight of flask full of water at 4° = 325.61 *g.*.

7. Applying Dulong and Petit's Law, calculate the specific heats of the following elements (their atomic weights are placed in parentheses): Aluminum (27), manganese (55), sodium (23), iron (56).

8. The specific heat of phosphorus is 0.189, and its vapor density referred to hydrogen is 62. How many atoms are there in a molecule of phosphorus gas?

SULFUR AND ITS COMPOUNDS

260. Occurrence. Sulfur occurs free principally in Sicily, Mexico, and Louisiana. Its compounds are numerous and widespread; the principal ones are iron bisulfid, FeS_2 (*pyrites*), lead sulfid, PbS (*galenite*), zinc sulfid, ZnS (*zinc blende*), antimony sulfid, Sb_2S_3 (*stibnite*), and hydrated calcium sulfate, $CaSO_4 + 2 H_2O$ (*gypsum*). It is also a constituent of some animal and vegetable products, as eggs, mustard, horseradish, onions, and garlic.

261. Preparation. Native sulfur is usually contaminated with earthy material. To free it from this, it is heaped up on sloping ground, in such a way that air can be admitted to the interior, covered over loosely with earth and set fire to. Somewhat less than half of the sulfur burns to furnish heat enough to melt the other half, which flows down and collects in wooden troughs, leaving the earthy impurities behind.

The sulfur thus obtained is purified by distillation; the vapor passes into a large condensing chamber, where some of the sulfur collects as a light powder, known as *flowers of sulfur*, while the rest collects in liquid form at the bottom and is drawn off into molds, giving the form of sulfur called *roll sulfur* or *brimstone*. *Lac sulfuris* or *milk of sulfur* is obtained by the action of hydrochloric acid on alkalin solutions of polysulfids.

262. Properties. *Physical.* (Table I., Appendix *D.*) Sulfur is a yellow solid, appearing nearly white when finely divided, without odor or taste. It is insoluble in water, but readily soluble in carbon bisulfid, excepting a few of its allotropic modifications. It is a non-conductor of electricity and a poor conductor of heat.

Chemical. Sulfur ignites at about 260° in the air, burning to sulfur dioxid, SO_2. It enters into combination with most elements at high temperatures, forming sulfids.

263. Allotropic Forms. Sulfur generally occurs in nature, and also crystallizes from its carbon bisulfid solution, in rhombs. Melted sulfur crystallizes in transparent, needle-shaped crystals which at ordinary temperatures change into the rhombic variety. Sulfur melts at 114° to a mobile, amber-colored liquid which at 170° assumes a darker color and becomes so thick and viscid as not to run out when the vessel containing it is inverted. At about 270° it turns darker still, but regains in part its mobility. If, just before it boils, it is suddenly cooled by pouring it into water, it forms a rubber-like mass. This *plastic sulfur* gradually turns into the rhombic form.

264. Uses. Sulfur is used in making sulfuric acid, matches, gunpowder, fireworks, in vulcanizing rubber, and in medicine.

HYDROGEN SULFID, H_2S (Sulfuretted Hydrogen)

265. Occurrence. Certain volcanic gases and the water from "sulfur springs" contain free hydrogen sulfid. It is also liberated by the decomposition of some animal substances, as eggs.

MENDELEEFF

MOISSAN

RAMSAY

DEWAR

Plate VI

HENRI MOISSAN

1852 —— ; French

Isolated fluorin. Perfected the electric furnace, and by its aid prepared artificial diamonds, rare metals, and compounds

DIMITRI IVANOVITCH MENDELEEFF

1834 —— ; Russian

Discovered the Periodic Law. Studied specific gravities of solutions and investigated geological chemistry

JAMES DEWAR

1842 —— ; English

Solidified hydrogen and is very active in applications of low temperatures to chemical problems

WILLIAM RAMSAY

1852 —— ; English

Active in physical and inorganic chemistry. Discovered argon, helium, neon, krypton, and xenon

Plate VI

266. Preparation. Hydrogen sulfid is prepared by the action of dilute sulfuric or hydrochloric acid on metallic sulfids; iron sulfid, FeS, is usually employed:

$$\text{FeS} + 2\,\text{HCl}\; or\; \text{H}_2\text{SO}_4 \rightarrow \text{FeCl}_2\; or\; \text{FeSO}_4 + \text{H}_2\text{S}$$
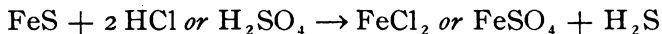
267. Properties. *Physical.* Hydrogen sulfid is a colorless gas of rather a sweet taste and a smell resembling that of rotten eggs. It is soluble in about a third its volume of water.

Chemical. Hydrogen sulfid burns with a blue flame:

$$2\,\text{H}_2\text{S} + 3\,\text{O}_2 \rightarrow 2\,\text{H}_2\text{O} + 2\,\text{SO}_2$$
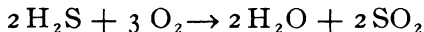
It is decomposed by the halogens with the separation of sulfur and the formation of the corresponding hydracid:

$$\text{H}_2\text{S} + \text{Cl}_2 \rightarrow 2\,\text{HCl} + \text{S}$$
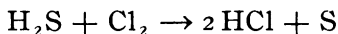
It acts upon many metallic salts with the formation of sulfids. Its aqueous solution decomposes readily when exposed to the air; the oxygen of the air combines with the hydrogen in the sulfid to form water, and the sulfur is set free. Air containing but a small proportion of it gives headache and nausea to the one breathing the mixture, while in larger proportions it produces unconsciousness and finally death.

COMPOSITION. Tin, heated in hydrogen sulfid gas, combines with the sulfur and leaves a volume of hydrogen equal to that of the gas taken. Hence, hydrogen sulfid contains an equal volume of hydrogen. Two volumes of hydrogen sulfid react with three volumes of oxygen to give two volumes of water vapor and two volumes of sulfur dioxid. This shows that two volumes of hydrogen sulfid contain two volumes of hydrogen,

for two volumes of hydrogen are contained in two volumes of water vapor.

HYDROGEN DISULFID, H_2S_2. Hydrogen disulfid is prepared by decomposing a polysulfid of calcium with dilute hydrochloric acid. It is a liquid with an odor similar to that of hydrogen sulfid, but much more penetrating. It is quite unstable, decomposing slowly into hydrogen sulfid and sulfur.

268. Sulfids. Sulfur combines with many other elements to produce *sulfids*. The union is often accompanied with the evolution of much heat and light, as, for example, in the case of iron and sulfur. Sulfids may also be prepared by passing hydrogen sulfid into solutions of metallic compounds, whereby, as all sulfids except those of the alkali and alkalin earth metals are insoluble in water, the metallic sulfids are precipitated. Hydrogen sulfid gas acts upon many metals, covering them with a coating of the respective sulfid. The tarnishing of silver is due to the action of the extremely minute amounts of this gas present in the air. Silver spoons are tarnished by the action of the sulfur compounds in mustard and eggs. Lead sulfid is black; hence houses painted with white lead paint often turn dark from the hydrogen sulfid in the air.

269. Carbon Bisulfid, CS_2. When sulfur vapor comes in contact with red-hot carbon (charcoal), union ensues, and a compound of the two elements, carbon bisulfid, CS_2, is produced. Carbon bisulfid is a colorless, mobile liquid, with a pleasant odor when pure, but when exposed to light it slowly decomposes into black, ill-smelling solids. It refracts light strongly and is used as a solvent for rubber and sulfur. Its ignition temperature is low

and the products of its combustion are sulfur dioxid and carbon dioxid:

$$CS_2 + 3\,O_2 \rightarrow CO_2 + 2\,SO_2$$
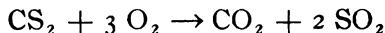
SULFUR DIOXID

270. Occurrence. Sulfur dioxid is found in most volcanic gases.

271. Preparation. The simplest method of preparing sulfur dioxid consists in burning sulfur or compounds rich in sulfur, as iron pyrites, FeS_2:

$$S + O_2 \rightarrow SO_2$$
$$4\,FeS_2 + 11\,O_2 \rightarrow 2\,Fe_2O_3 + 8\,SO_2$$
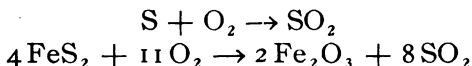
Copper and some other metals when heated with strong sulfuric acid decompose it with liberation of sulfur dioxid. So also does carbon, thus:

$$C + 2\,H_2SO_4 \rightarrow CO_2 + 2\,SO_2 + 2\,H_2O$$
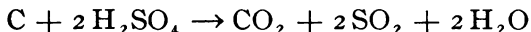
A convenient method consists in the action of dilute hydrochloric acid on sodium sulfite, Na_2SO_3:

$$Na_2SO_3 + 2\,HCl \rightarrow 2\,NaCl + H_2O + SO_2$$
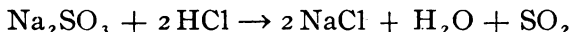
272. Properties. *Physical.* Sulfur dioxid is a colorless gas of suffocating odor, and heavy enough to be collected by downward displacement like carbon dioxid. Water dissolves about fifty times its own volume of it. The gas may be converted into a colorless liquid at the temperature of a freezing mixture of ice and salt and this liquid at $-76°$ turns into a transparent solid.

Chemical. Sulfur dioxid is a non-supporter of combustion in general, but ignited potassium or magnesium continue to burn in it, and finely divided metals, as iron, will even take fire when introduced

into it. Its aqueous solution has acid properties, and it is probable that sulfurous acid, H_2SO_3, is formed.

COMPOSITION. When sulfur is burned, the volume of the resulting sulfur dioxid is equal to that of the oxygen used. Hence, equal volumes of sulfur vapor and oxygen are contained in it.

273. Uses. Sulfur dioxid is used in enormous quantities in the manufacture of sulfuric acid. Its use as a disinfectant is well known (sulfur candles). It is also used in bleaching and in paper-making.

BLEACHING. Sulfur dioxid bleaches, not by destroying the coloring matter, but by forming with it a colorless compound. This compound is decomposed by sulfuric acid or an alkali, and the original color restored. A red rose turns white when held in the gas, but its color is restored by dipping it in very dilute sulfuric acid. The bleaching effect also disappears after a time, so that cloth and straw bleached by sulfur dioxid "yellow" with age.

274. Sulfur Trioxid. Sulfur trioxid is obtained by heating fuming sulfuric acid, or by passing a mixture of sulfur dioxid and oxygen over heated platinized asbestos. It forms a white, crystalline solid which melts at 16°. When placed in water it dissolves with a hissing noise and forms sulfuric acid.

COMPOUNDS OF SULFUR, OXYGEN, AND HYDROGEN

275. Sulfur, in combination with varying proportions of oxygen and hydrogen, forms several acids, of which only sulfuric acid, H_2SO_4, is important.

SULFUROUS ACID, H_2SO_3. Sulfurous acid is formed when sulfur dioxid is dissolved in water. It is quite unstable, and is converted into sulfuric acid by standing

exposed to the air for some time. It forms several important and stable salts, however.

SULFURIC ACID

HISTORICAL NOTE. Sulfuric acid has been known since the eighth century, when it was prepared by distilling green vitriol (ferrous sulfate). Towards the end of the eighteenth century the "lead-chamber method" of manufacture was devised, and within the last few years the "contact process" has been perfected.

276. Occurrence. Free sulfuric acid is found in small quantities in the water of some rivers whose sources are in volcanic districts. Its compounds with metals, the sulfates, are quite common; gypsum, a sulfate of calcium, $CaSO_4$, is especially abundant.

277. Preparation. Sulfuric acid is never prepared in the laboratory except as an illustration of the industrial process. The principle of this process consists in the oxidation of sulfur dioxid to trioxid and the union of the latter with water. The conversion of the dioxid into the trioxid is effected by means of platinized asbestos or the higher oxids of nitrogen. These give up a portion of their oxygen to sulfur dioxid, and immediately take it up again from the air, which must always be present. The nitrogen compounds thus act as carriers of oxygen from the air to the sulfur dioxid. Theoretically, a very small amount of them should suffice to oxidize a very large amount of the sulfur dioxid, but practically there is a limit to the amount.

THEORY OF THE PROCESS. Several theoretical explanations of the process of oxidation have been advanced, of which that due to Lunge is perhaps the most satisfactory. He assumes that the sulfur dioxid combines

PYRITES BURNERS · STILL · STRONG ACID BLOWER · CONCENTRATING PANS · NITER-ACID BLOWER

GLOVER TOWER · STEAM · CHAMBER 1 · CHAMBER 2 · CHAMBER 3 · CHAMBER 4 · GAY LUSSAC TOWER
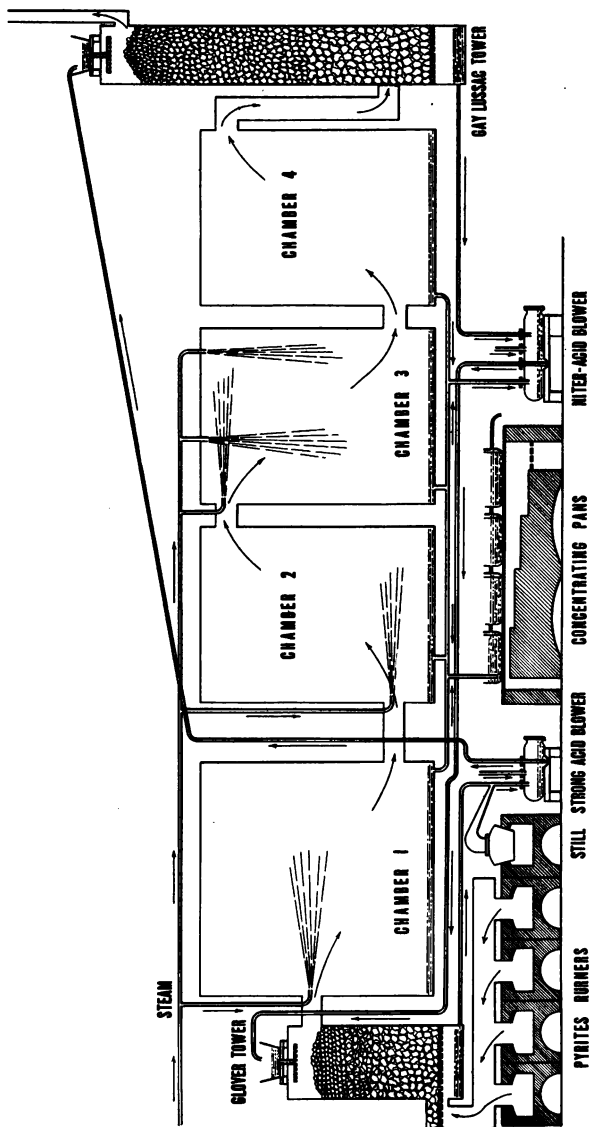
Fig. 35 — APPARATUS FOR PREPARING SULFURIC ACID ON A LARGE SCALE

with the oxids of nitrogen and water to form nitrosyl-sulfuric acid, $SO_2(NO_2)OH$, so called from *nitrosyl*, the name of the radical NO_2.

$$SO_2 + HNO_3 \rightarrow SO_2(NO_2)OH$$
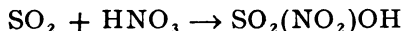
This reacts with steam thus :

$$2 SO_2(NO_2)OH + H_2O \rightarrow 2 H_2SO_4 + NO + NO_2$$
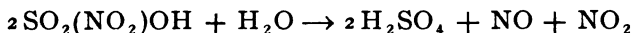
The nitrogen oxids react with more sulfur dioxid, oxygen (from the air), and steam :

$$2 SO_2 + NO + NO_2 + O_2 + H_2O \rightarrow 2 SO_2(NO_2)OH$$
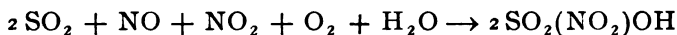
The nitrosyl-sulfuric acid thus formed is decomposed by steam as above, and these reactions repeat themselves. The process becomes continuous and the oxids of nitrogen are used again and again.

278. Practice of the Process. (Fig. 35.) The sulfur dioxid is obtained by burning sulfur or iron pyrites, FeS_2, in a suitable furnace. The dioxid mixed with air passes from the furnace at a temperature of about 300° into the bottom of a tall tower, called "Glover's tower," which is lined with lead and filled with large fragments of brick below and smaller pieces of coke above. Down this tower trickles dilute sulfuric acid mixed with nitric acid and nitrogen oxids ("niter-acid"). As the hot gases rise they carry off with them as vapor most of the water and nitrogen compounds dissolved in the sulfuric acid, so that a "strong acid" free from nitrogen compounds flows out at the base of the tower.

By passing through the "Glover" the mixture of gases is cooled down to about 70°, the temperature which is most favorable for the oxidation of the sulfur dioxid.

On leaving the "Glover" the gaseous mixture passes into the first of three or four immense chambers lined with lead, into which steam is blown. The oxidation takes place as the gases pass through the chambers and the sulfuric acid formed collects at the bottom of the chambers, where it is drawn off from time to time. The oxidation is almost complete when the gases leave the second chamber. No steam is blown into the last chamber, so that the residual gases may cool off a little.

The gases escaping from the last chamber contain nitrogen compounds which are caught in another tower, called "Gay-Lussac's tower." Down the coke with which it is filled trickles concentrated sulfuric acid, which dissolves out the nitrogen compounds in the ascending gases. Only the waste gases, such as the nitrogen from the air used in the burning of the pyrites, escape from the "Gay-Lussac" into the chimney which causes the draft through the chambers. The acid collecting at the base of the "Gay-Lussac" is forced up into a tank above the "Glover," by means of compressed air, and its nitrogen compounds as well as most of its water removed by flowing down the "Glover" as stated above. The process is thus seen to be continuous. The acid obtained from the lead chambers is called "chamber acid," and contains about 35 per cent of water. This is strong enough for many uses, but most of it is concentrated in lead or cast-iron pans until it contains about 23 per cent of water, when, as the acid now begins to act upon the metal, its further concentration is effected by heating it in platinum vessels.

MANUFACTURE BY THE CONTACT METHOD. Although it has been known for many years that sulfur trioxid is formed when a mixture of sulfur dioxid and oxygen (air) is passed over heated platinized asbestos, the commercial application of the process was hindered by the fact that the catalytic agent soon lost its efficacy. Recently, however, it has been found that by thoroughly washing the gaseous mixture, the life of the platinized asbestos and also of other "catalyzers" can be prolonged so as to make the process of commercial value. Another difficulty in the process that had also to be overcome was the delicate regulation of the temperature required. The contact process is being introduced rapidly into chemical works and bids fair to become a serious competitor of the lead-chamber process.

279. Properties. *Physical.* Sulfuric acid is a thick, colorless liquid of oily appearance. It mixes in all proportions with water, and the mixing is accompanied with the evolution of much heat. To avoid spattering the acid should be poured slowly *into the water*, never the water into the acid. When exposed to the air it absorbs the water vapor which may be present with great avidity, and thus makes an excellent drying agent.

Chemical. Most animal and vegetable substances are charred by strong sulfuric acid, which removes in part the elements of water. At a red heat the acid decomposes into sulfur dioxid, oxygen, and water vapor; at temperatures near its boiling point it dissociates into water and sulfur trioxid to a limited extent. It neutralizes bases and chemically dissolves most metals, the sulfates of which are thus formed, and hydrogen or sulfur dioxid are evolved according to the conditions of temperature, concentration of the acid, and nature of the metal.

280. Uses. Sulfuric acid is undoubtedly the most useful "chemical"; it is employed in almost all chemical industries. It is necessary in the manufacture of hydrochloric (§ 202) and nitric (§ 174) acids, of sodium carbonate (§ 225), of fertilizers, of glucose, and many other products.

281. Fuming or Pyrosulfuric Acid. When iron pyrites, FeS_2, is exposed to the weather it gradually takes up oxygen and becomes partially converted into iron sulfate, $Fe_2(SO_4)_3$. This is leached out, evaporated to dryness, and heated to a high temperature in earthenware retorts. Sulfur trioxid and iron oxid are the products, of which the latter remains in the retort and the former distills over into receivers containing water:

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3\,SO_3$$
$$H_2O + 2\,SO_3 \rightarrow H_2S_2O_7$$
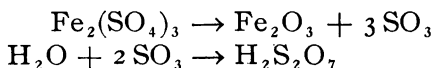
This acid, sometimes called "Nordhausen oil of vitriol," is probably a solution of sulfur trioxid in sulfuric acid, for it readily yields these compounds when heated. It is an even more energetic acid than sulfuric. It gives off fumes of sulfur trioxid when exposed to the air. Pyrosulfuric acid is now almost exclusively manufactured by the "contact process."

THIOSULFURIC ACID. Oxygen and sulfur resemble each other in many particulars, and sulfur may replace oxygen in several compounds. Thiosulfuric acid, $H_2S_2O_3$, may then be regarded as sulfuric acid, H_2SO_4, in which one-fourth of the oxygen has been replaced by sulfur. This acid has not yet been obtained in a pure state, but some of its salts are known; sodium thiosulfate, $Na_2S_2O_3$, commonly but erroneously known as

"hyposulfite of soda," is the most important because of its use in dyeing and photography.

Exercises

1. What are the general methods of preparing sulfids?

2. What acids form white fumes when ammonia is brought near them? Why?

3. Given strong ammonia water, how can you ascertain whether or not sulfuric acid is volatile?

4. What would you think would be produced by heating solid ammonium sulfid, $(NH_4)_2S$?

5. Devise simple and rapid tests for distinguishing sodium carbonate, sodium sulfate, sodium sulfid, and sodium formate from one another.

6. What is the objection to concentrated sulfuric acid as a drying agent for ammonia? What compound can be used to dry ammonia?

7. In the electrolysis of dilute sulfuric acid why is oxygen given off at the anode?

Problems

1. 100 *c.c.* of hydrogen sulfid are burned. What gases result, and how many cubic centimeters of each?

2. How many cubic centimeters of sulfur can be obtained from 100 *c.c.* of sulfur vapor, the temperature of which is 500°?

3. How many grams of ferrous sulfid are required to prepare 10 *l.* of hydrogen sulfid?

4. How much oxygen, both by weight and volume, is required to burn 100 *g.* of sulfur containing 12% of incombustible impurities?

5. If the specific gravity of sulfuric acid is 1.8, how many cubic centimeters of the acid will a liter flask contain?

6. What weight and what volume of hydrogen can be obtained from 5.1 *g.* of hydrogen sulfid?

7. Berzelius, in 1818, converted 10.000 *g.* of lead into 14.642 *g.* of lead sulfate, $PbSO_4$. The atomic weights of lead and of oxygen are 206.91 and 16.00. Calculate the atomic weight of sulfur.

8. Dumas, in 1859, synthesized silver sulfid, Ag_2S, finding the ratio of the weights of silver and of the sulfid to be 112.1943 : 128.8288. The atomic weight of silver is 107.94; find the atomic weight of sulfur.

PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

The elements phosphorus, arsenic, antimony, and bismuth not only exhibit certain similarities among themselves, but also with nitrogen. They may, therefore, be studied with advantage together. In this natural family there is a gradual transition. from the non-metals to the metals. Both in physical and in chemical properties, nitrogen and phosphorus are typical non-metals. Arsenic begins to present metallic properties, while antimony is decidedly metallic in character, and bismuth has no non-metallic properties at all.

PHOSPHORUS

HISTORICAL NOTE. Phosphorus was first prepared by Brande in 1669. He kept his method secret at first, but Kunckel found out what substance was used in its preparation and shortly afterward succeeded in making it also. Scheele a century later invented the process used in manufacturing phosphorus from the ashes of bones.

282. Occurrence. Phosphorus is never found free in nature, but certain of its compounds are quite abundant and widely diffused. Calcium phosphate, $Ca_3(PO_4)_2$, is found in many places as large deposits of the minerals *phosphorite* and *apatite*, also in guano deposits and in the ashes of bones.

283. Preparation. Finely ground bone ash or natural phosphates are treated with dilute sulfuric acid, whereby the insoluble phosphate is converted into a soluble phosphate, commonly called *superphosphate of lime*, and much used as a fertilizer. The reaction is:

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \rightarrow CaH_4(PO_4)_2 + 2\,CaSO_4$$
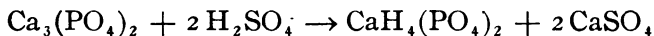
The solution of the acid calcium phosphate, $CaH_4(PO_4)_2$, is filtered from the insoluble calcium sulfate, $CaSO_4$, evaporated to dryness, and the product strongly heated. Water is thus driven off and calcium metaphosphate formed:

$$CaH_4(PO_4)_2 \rightarrow Ca(PO_3)_2 + 2\,H_2O$$

This is mixed with charcoal and distilled in clay retorts at a very high temperature. The phosphorus formed vaporizes and is condensed into a liquid under warm water in a receiver.

$$3\,Ca(PO_3)_2 + 10\,C \rightarrow P_4 + Ca_3(PO_4)_2 + 10\,CO$$
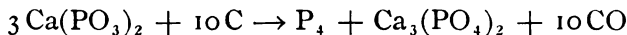
The product is purified by redistillation or by treatment with a solution containing sulfuric acid and potassium dichromate. It is then filtered through canvas and cast into sticks.

ELECTRO-CHEMICAL PROCESS. Natural calcium phosphate is intimately mixed with carbon and sand, and placed in a retort-like furnace heated inside by a powerful electric current passing between carbon electrodes. The phosphorus distills off and is condensed under water.

284. Properties. *Physical.* (Table I., Appendix *D*.) Phosphorus, when freshly prepared, is a translucent, almost colorless, waxy solid. It loses

its translucency, however, even in the dark, and when exposed to light turns darker and darker in color; an allotropic modification (red or amorphous phosphorus) is formed. It is somewhat volatile at ordinary temperatures. Its vapor density is 62, which shows that its molecule consists of four atoms, or is tetratomic. At temperatures above 1,000° this tetratomic molecule begins to dissociate. Phosphorus is insoluble in water, but very soluble in carbon bisulfid.

Chemical. Phosphorus takes fire very readily, and is hence preserved and handled under water, which protects it from the oxygen of the air. It burns to white phosphorus pentoxid, P_2O_5. It combines with the halogens even at ordinary temperatures, and with many other elements; its metallic compounds are called *phosphids*. It is very poisonous, and persons engaged in handling it, in its manufacture, or in that of matches, are liable to be attacked by serious diseases of the nose and jaw.

285. Red Phosphorus. If waxy phosphorus be heated with exclusion of air or oxygen to about 250°, it changes into a dark red, amorphous mass. This allotropic form has no odor, is insoluble in carbon bisulfid, is not phosphorescent, is not poisonous, and has a rather high kindling point. When heated above 300° it changes back into the ordinary form.

286. Uses. Phosphorus is used in the manufacture of matches and vermin poisons. Phosphates are employed in fertilizers, medicines, and some baking powders.

MATCHES. Matches consist of light wood sticks tipped with waxy phosphorus mixed with certain substances that yield oxygen readily when heated. Phosphorus, together with lead dioxid, potassium nitrate or chlorate, or mixtures of these compounds, is ground up under water containing a little gum. The ends of the match sticks, previously coated with sulfur or paraffin, are pressed into this mixture and then dipped into a solution of gum and shellac to protect the phosphorus from the oxygen of the air. When such a match is rubbed over a rough surface, the gummy coating is scratched off, and the heat due to the friction is sufficient to set on fire the phosphorus which burns at the expense of the oxygen in the other ingredients. The sulfur or paraffin is ignited and then the wood.

"Safety" or Swedish matches do not contain any phosphorus and hence are not poisonous, and do not take fire from friction except on a prepared surface consisting of a mixture of red phosphorus, fine sand, and gum, applied usually to the sides of the boxes in which the matches are packed. These matches are tipped with a very combustible compound, antimonious sulfid, Sb_2S_3, mixed with potassium chlorate and dichromate and red lead. The friction on the prepared surface raises the temperature enough to ignite the red phosphorus which, while it does not burn in the surface, sets on fire the combustible material on the stick.

ARSENIC

HISTORICAL NOTE. The sulfid ores of arsenic have been known from the earliest times, and the alchemists knew how to prepare the white oxid by roasting these ores. This oxid was long called arsenic, and it was not until towards the end of the eighteenth century that it was proved to be a compound of arsenic and oxygen.

287. Occurrence. Arsenic occurs free in small quantities in a few places. Its main natural compounds are *arsenopyrite*, FeSAs, *realgar*, As_2S_2, and *orpiment*, As_2S_3.

288. Preparation. Arsenopyrite is heated in long earthenware retorts, placed horizontally and fitted with earthenware receivers. The pyrite decomposes:

$$2\,FeSAs \rightarrow 2\,As + 2\,FeS$$
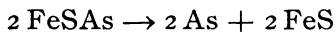
The arsenic volatilizes and condenses in the receivers as a compact mass and is purified by distillation. It may also be prepared by heating arsenious oxid with charcoal:

$$As_4O_6 + 6\,C \rightarrow 4\,As + 6\,CO$$
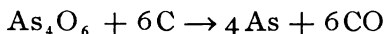
289. Properties. *Physical.* (Table I., Appendix *D*.) Free arsenic resembles metals in being opaque, rather heavy, and of a metallic luster. It is steel gray in color, very brittle, and a good conductor of heat and electricity. It begins to sublime at about 100°, producing a yellow, ill-smelling vapor, the vapor density of which is about $300 = (4 \times 75)$. Its molecule consists of four atoms and its formula is As_4. At high temperatures the As_4 molecules dissociate into As_2 molecules.

Chemical. When heated in oxygen to about 180°, arsenic burns with a bright bluish-white flame, forming arsenious oxid, As_4O_6. It combines readily with the halogens.

290. Uses. Arsenic in small proportion forms with lead an alloy which is more fusible and harder than lead. This alloy is used in making shot.

ANTIMONY

HISTORICAL NOTE. Antimony was investigated with great care in the fifteenth century by a monk, Basil Valentine, who published his results in a book bearing the title of *The Triumphal Chariot of Antimony*.

291. Occurrence. Antimony is found in small amounts in a few places, but it is generally obtained from its mineral, *stibnite* or *gray antimony ore*, Sb_2S_3.

292. Preparation. I. Stibnite is roasted, and the resulting oxid reduced with carbon :

$$Sb_2S_3 + 5 O_2 \rightarrow Sb_2O_4 + 3 SO_2$$
$$Sb_2O_4 + 4 C \rightarrow 2 Sb + 4 CO$$
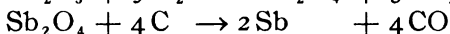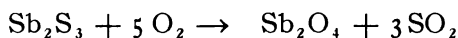
II. Stibnite is heated with scrap iron in plumbago crucibles. The sulfur leaves the antimony to unite with the iron, and as the molten antimony is heavier than, and does not mix with the iron sulfid, it sinks to the bottom and may there be drawn off :

$$3 Fe + Sb_2S_3 \rightarrow 3 FeS + 2 Sb$$
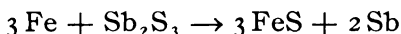
293. Properties. *Physical.* (Table I., Appendix *D.*) Antimony is a bluish-white solid with a brilliant metallic luster, and does not tarnish at ordinary temperatures. It expands at the moment of solidification, and is on that account made one of the ingredients of type metal, to which it imparts the property of taking sharp castings. It is so brittle as to be easily pulverized. Its gaseous molecule has the formula Sb_2.

Chemical. Antimony burns in the air with a white flame, yielding dense fumes of antimonious oxid, Sb_2O_4, and combines readily with the halogens. Dilute sulfuric and hydrochloric acid are without action upon it, while the concentrated acids convert it into the sulfate and chlorid, respectively. It is oxidized by nitric acid.

294. Uses. Antimony is chiefly employed in making certain alloys, such as type metal, Britannia metal, white metal, and Babbitt metal.

17

BISMUTH

HISTORICAL NOTE. Although bismuth has been known since the third century, it was confounded with antimony, and it was not until the middle of the eighteenth century that its true nature and properties were recognized.

295. Occurrence. Bismuth occurs native in the veins of certain crystalline rocks, and most of the commercial supply is obtained from this source. Its oxid, Bi_2O_3 (*bismuth ochre*), and sulfid, Bi_2S_3 (*bismuthinite*), are also found.

296. Preparation. Native bismuth is heated in inclined iron pipes. The bismuth melts and runs off, leaving most of the impurities behind. Such a process is called "liquation."

297. Properties. *Physical.* (Table I., Appendix *D*.) Bismuth is a lustrous white metal with a reddish tinge. It is brittle and but slightly ductile and malleable.

Chemical. Bismuth burns with a bluish flame, and combines readily with the halogens. It is insoluble in dilute hydrochloric and sulfuric acid, but easily soluble in nitric acid and hot concentrated acids.

298. Uses. Bismuth forms valuable alloys with other metals, imparting to them hardness and fusibility. Wood's metal and Rose's metal are alloys which melt below 100°.

OXYGEN COMPOUNDS

299. The Oxids. Phosphorus, arsenic, antimony, and bismuth each form several oxids, the most important of which are the trioxids and pentoxids, corresponding to the general formulas M_2O_3 and M_2O_5, where M denotes any one of the elements.

The oxids are white or light yellow powders, and most of them combine with water to form acids.

300. Phosphorus Trioxid, P_2O_3.   Phosphorus trioxid is formed by burning phosphorus in a limited supply of oxygen. It is a white powder, smelling like garlic, and soluble in water.

301. Phosphorus Pentoxid, P_2O_5.   Phosphorus pentoxid is prepared by burning phosphorus in an abundance of oxygen. It is a soft, light, white powder, very soluble in water. It absorbs water from gases eagerly, and hence is used as a drying agent.

302. Arsenious Oxid or Arsenic Trioxid, As_4O_6. Arsenious oxid or arsenic trioxid is obtained as a by-product in the roasting of certain arsenical pyrites. It is a white powder, which, when sublimed, yields glass-like masses (the vitreous modification). It is somewhat soluble in water, quite so in dilute hydrochloric acid and sodium hydroxid solutions.

Arsenic trioxid, commonly known as *white arsenic,* or simply arsenic, is the most abundant commercial compound of arsenic. It has a slightly sweetish taste, and is very poisonous, if not more than 0.02 $g.$ be taken. Larger doses act as an emetic, while very small doses act as a tonic. The antidote is freshly prepared ferric hydroxid or magnesia. At temperatures from 200° to above 700° the molecule As_4O_6 dissociates into As_2O_3 molecules.

ARSENIC OXID OR PENTOXID, As_2O_5. Arsenic oxid is formed by heating arsenious oxid with strong nitric acid:

$$As_2O_3 + 2\,HNO_3 \rightarrow As_2O_5 + NO + NO_2 + H_2O$$
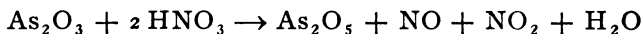
The products of the reaction when heated to about 300° yield the pure pentoxid ; when to a red heat, the trioxid and oxygen result.

ANTIMONY TRIOXID, Sb_2O_3. Antimony trioxid results when antimony is oxidized with dilute nitric acid. It is a white, almost insoluble powder.

ANTIMONY PENTOXID, Sb_2O_5. Antimony pentoxid is obtained by oxidizing antimony with strong nitric acid. It is a light yellow powder, slightly soluble in water.

ANTIMONY TETROXID, Sb_2O_4. Antimony tetroxid is formed by heating either the trioxid or the pentoxid in air. It is a white powder, insoluble in water.

BISMUTH OXIDS. Of the four oxids of bismuth known, Bi_2O_2, Bi_2O_3, Bi_2O_4, Bi_2O_5, the trioxid is the most important. It is a yellow powder, used in making some sorts of glass.

ARSENIC SULFIDS. Two sulfids of arsenic are found as minerals, realgar, As_2S_2, and orpiment, As_2S_3. Artificial realgar may be made by subliming a mixture of arsenical and iron pyrites. It is a red glassy mass used as a pigment. By subliming a mixture of arsenious oxid and sulfur, artificial orpiment, known as "King's yellow," is obtained. The trisulfid may also be prepared by precipitating a solution of arsenic by hydrogen sulfid. Arsenic pentasulfid, As_2S_5, is obtained by fusing the trisulfid and sulfur together.

ANTIMONY SULFIDS. Antimony trisulfid, Sb_2S_3, occurs in nature as the mineral stibnite, and may be prepared by passing hydrogen sulfid into a solution of antimony trichlorid; it is precipitated as an orange-yellow powder, soluble in solutions of alkalin sulfids. The pentasulfid is formed by precipitating a solution of antimony pentachlorid, $SbCl_5$, with hydrogen sulfid. It is dark orange in color and is soluble in alkalin sulfids.

BISMUTH TRISULFID, Bi_2S_3. Bismuth trisulfid is the only sulfid of bismuth, and occurs as the mineral, bismuth glance. It is formed as an almost black precipitate when hydrogen sulfid is passed into a solution of a bismuth salt.

HYDROGEN COMPOUNDS

Arsenic, antimony, and phosphorus unite with hydrogen to form gaseous compounds of constitution similar to that of ammonia. They are all

colorless, poisonous gases, with a very disagreeable odor, and are but slightly soluble in water.

303. Phosphin, PH_3. (*Hydrogen Phosphid, Phosphoretted Hydrogen.*) Phosphin is made by heating phosphorus with a strong solution of potassium hydroxid. A small amount of a liquid compound of phosphorus and hydrogen, P_2H_4, is also formed, and the mixture burns on coming in contact with the air. If the P_2H_4 be removed by passing the mixture through a tube surrounded with a freezing mixture, the pure PH_3 is found not to be spontaneously combustible. Phosphin may also be prepared by the action of water on calcium phosphid.

ARSIN, AsH_3, HYDROGEN ARSENID. (*Arseniuretted Hydrogen.*) Arsin is formed whenever nascent hydrogen can react upon any soluble arsenical compound. It is readily decomposed by heat into hydrogen and arsenic.

STIBIN, SbH_3, HYDROGEN ANTIMONID. (*Antimoniuretted Hydrogen.*) Stibin is made like arsin, by substituting any soluble compound of antimony.

HALOGEN COMPOUNDS

304. Phosphorous Chlorids. Phosphorous chlorids are prepared by passing a current of dry chlorin over phosphorus. At first the trichlorid, PCl_3, a colorless liquid, forms, but as the action of the chlorin continues, the pentachlorid, PCl_5, a yellow solid, appears. The pentachlorid decomposes into the trichlorid and chlorin when heated. The bromids and iodids of phosphorus are quite similar to the chlorids.

THE HALOGEN COMPOUNDS OF ARSENIC, ANTIMONY, AND BISMUTH. The halogen compounds of arsenic, antimony, and bismuth resemble in modes of preparation, properties, and reactions those of phosphorus.

ACIDS AND SALTS

305. Hypophosphorous Acid. Hypophosphorous acid, H_3PO_2, is prepared as follows: Phosphorus is boiled with a solution of barium hydroxid, $Ba(OH)_2$, whereby phosphin and barium hypophosphite, $Ba(H_2PO_2)_2$, are formed. Sulfuric acid is then added in quantity just sufficient to precipitate all the barium as insoluble barium sulfate, $BaSO_4$, leaving the hypophosphorous acid in solution:

$$Ba(H_2PO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_3PO_2$$
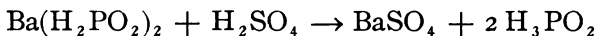
Hypophosphorous acid is a white, crystalline solid, melting at 170°, which, when strongly heated, is converted into phosphin and orthophosphoric acid:

$$2H_3PO_2 \rightarrow H_3PO_4 + PH_3$$
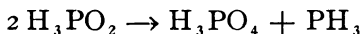
Although orthophosphoric acid contains three hydrogen atoms, but one is replaceable by a univalent base or basic radical; it acts as a monobasic acid.

306. Phosphorous Acid, H_3PO_3 or $P(OH)_3$. Phosphorous acid is formed when phosphorous oxid is dissolved in water:

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$
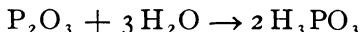
or when phosphorous trichlorid, PCl_3, is acted upon by water:

$$PCl_3 + 3H_2O \rightarrow P(OH)_3 + 3HCl$$
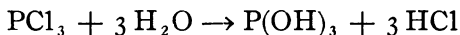
The formation and decomposition of phosphorus trichlorid may be effected simultaneously by passing a current of chlorin into melted phosphorus under hot water. Phosphorous acid is a white, crystalline solid, melting at 70°, and when heated decomposes into orthophosphoric acid and phosphin:

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

Although a tribasic acid, its tribasic salts are unstable. The monobasic and dibasic salts, however, are stable.

Both hypophosphorous and phosphorous acids are strong reducing agents; they absorb oxygen eagerly and are thus converted into orthophosphoric acid.

307. Orthophosphoric Acid, H_3PO_4. Orthophosphoric acid is formed when phosphorus pentoxid is dissolved in boiling water, and when red phosphorus is oxidized by means of nitric acid. It is a white, crystalline solid, melting at 39°. It forms three series of salts.

308. Pyrophosphoric Acid, $H_4P_2O_7$. Pyrophosphoric acid is obtained from orthophosphoric acid by heating it to about 200°:

$$2\,H_3PO_4 - H_2O \rightarrow H_4P_2O_7$$
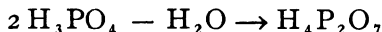
309. Metaphosphoric Acid, HPO_3. Metaphosphoric acid may be obtained by heating orthophosphoric or pyrophosphoric acid to redness:

$$H_3PO_4 - H_2O \rightarrow \ HPO_3$$
$$H_4P_2O_7 - H_2O \rightarrow 2\,HPO_3$$
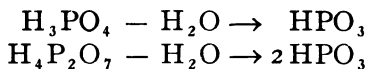
It is a glassy solid and is frequently called "glacial phosphoric acid." In solution it gradually changes into orthophosphoric acid. It is monobasic.

310. Phosphates and Their Uses. Soluble phosphates are essential to plant life. The normal phosphate of calcium, $Ca_3(PO_4)_2$, found in bone-ash and in nature, being insoluble in water, must first be converted into a soluble phosphate that it may be taken up by plants. By the action of dilute sulfuric acid the normal phosphate is converted into

primary calcium phosphate, $Ca(H_2PO_4)_2$, which is soluble. This "superphosphate of lime" is much used as a fertilizer and also as the acid constituent of phosphatic baking powders.

ARSENIC ACIDS AND SALTS. Arsenious acids have never been obtained, but three series of *arsenites* corresponding to three hypothetical acids, *ortho-arsenious acid*, H_3AsO_3, *pyro-arsenious acid*, $H_4As_2O_7$, and *meta-arsenious* acid, $HAsO_3$, are known. All but the alkalin arsenites are insoluble in water, and when heated are converted into arsenic and arsenates. Arsenic pentoxid dissolves in water, forming *ortho-arsenic* acid, H_3AsO_4. By heating this the *pyro-* and *meta-arsenious acids*, $H_4As_2O_7$ and $HAsO_3$, may be obtained. All three acids are crystalline solids and form salts resembling those of the corresponding phosphorous acids.

ARSENIC GREENS. Two arsenic compounds have a bright green color — "Scheele's green," which is copper arsenite, and "Schweinfurt's green," a mixture of copper arsenite and copper acetate. Both are known commercially as "Paris green." Their use as dyes, which was formerly quite general, has been discontinued because of their poisonous qualities and because harmless substitutes have since been discovered. The use of Paris green to kill potato bugs is familiar.

ANTIMONY ACIDS AND SALTS. Ortho-, pyro-, and meta-antimonic acids, H_3SbO_4, $H_4Sb_2O_7$, and $HSbO_3$, are known and resemble the corresponding acids of phosphorus and arsenic. Meta- and pyro-antimoniates are found, but no ortho-antimoniates are known.

Exercises

1. What objection is there to the use of arsenic greens for coloring wall papers?

2. Why is the arsenic vapor molecule supposed to consist of four atoms?

3. Why is not phosphorus used for illuminating purposes?

4. What class of substances is formed by the action of water on the products of the combustion of non-metals?

5. What practical value have low-melting alloys?

Problems

1. How much phosphorus is there in a ton of bone-ash if 68 per cent of the ash is calcium phosphate, $Ca_3(PO_4)_2$?

2. How much sulfur dioxid can be obtained from 1,000 pounds of stibnite, Sb_2S_3 ?

3. How much sulfur is combined with 100$g.$ of realgar, As_2S_2, and of orpiment, As_2S_3, respectively? What is the simplest ratio of these amounts?

4. How much bone-ash containing 68 per cent of calcium phosphate, $Ca_3(PO_4)_2$, must be employed to make a ton of the fertilizer, superphosphate of lime?

5. If one million matches can be tipped with one pound of phosphorus, how much phosphorus does your family use in a year?

6. If a skeleton weighs 21 pounds and contains 56 per cent of $Ca_3(PO_4)_2$, how many matches can be tipped with the phosphorus it contains, if one pound of phosphorus serves to tip a million matches?

7. How much greater is the percentage of phosphorus in calcium metaphosphate, $Ca(PO_3)_2$, than in calcium orthophosphate, $Ca_3(PO_4)_2$?

8. At 236° phosphorus pentachlorid dissociates into phosphorus trichlorid and free chlorin. What is the volume of the mixed gases when 10$l.$ of the pentachlorid dissociate?

9. If the specific gravity of phosphorus is 1.84, what is the weight of a cylindrical stick of it 25$cm.$ long and 0.8$cm.$ in diameter?

10. Calculate the percentage composition of sodium phosphate, Na_3PO_4, and of disodium phosphate, HNa_2PO_4.

11. What is the loss in the weight of a stick of phosphorus which has been employed to remove the oxygen from 54.8$c.c.$ of air at 20° and 746$mm.$?

12. Van der Plaats, in 1885, obtained by burning 18.5854$g.$ of phosphorus, 42.5840 $g.$ of phosphorus pentoxid. If the atomic weight of oxygen is taken as 16.00, what is the atomic weight of phosphorus?

13. Dumas, in 1859, decomposed 11.454$g.$ of phosphorus trichlorid with water, precipitated with silver nitrate, and found 26.978$g.$ of silver in the precipitate. Write the equations for the reactions involved and calculate the atomic weight of phosphorus. The atomic weights of chlorin and silver are 35.45 and 107.94, respectively.

14. Cooke, in 1878, precipitated the bromin in 13.2659 g· of antimony tribromid as silver bromid, obtaining 11.9391 g· of silver. Taking the atomic weights of bromin and silver as 79.96 and 107.94, respectively, calculate the atomic weight of antimony.

15. Schneider, in 1856, heated antimony sulfid, Sb_2S_3, in a hydrogen atmosphere and weighed the sulfur given off as well as the antimony. The results of three determinations were:

	I	II	III
Antimony,	1.49916	2.99091	5.85754
Sulfur,	0.59890	1.19495	2.33959

From these data calculate the atomic weight of antimony; the atomic weight of sulfur is 32.06.

16. Dumas, in 1859, precipitated the chlorin in 22.173 g· of arsenic trichlorid with silver nitrate solution and found 39.597 g· of silver in the silver chlorid thrown down. The atomic weights of chlorin and silver are 35.45 and 107.94, respectively; what is the atomic weight of arsenic?

17. Marignac, in 1884, by reducing in hydrogen obtained from 29.5035 g· of bismuth oxid, Bi_2O_3, 3.0440 g· of oxygen. Calculate the atomic weight of bismuth, taking the atomic weight of oxygen as 16.00.

18. Marignac also converted 16.6450 g· of bismuth oxid into 25.2551 g· of bismuth sulfate, $Bi_2(SO_4)_3$. The atomic weight of sulfur is 32.06. Calculate that of bismuth.

CHAPTER XXIII

THE ALKALIN EARTH METALS AND THEIR COMPOUNDS

The metals *beryllium*, *magnesium*, *calcium*, *strontium*, and *barium* form a well-defined group of elements; the properties of the three last are especially similar. Beryllium, formerly called *glucinum* because of the sweet taste of some of its salts, is rare and resembles magnesium very closely. All these metals are bivalent. The calcium, strontium, and barium hydroxids are strong bases and have an earthy appearance; hence the name of *alkalin earths*.

311. Occurrence. The alkalin earth metals are never found free in nature, but certain of their compounds, especially the sulfates and carbonates, are very abundant, as calcium carbonate, $CaCO_3$ (*calcite*, *marble*, and *limestone*), calcium sulfate, $CaSO_4$ (*selenite*), strontium carbonate, $SrCO_3$ (*strontianite*), strontium sulfate, $SrSO_4$ (*celestite*), barium carbonate, $BaCO_3$ (*witherite*), barium sulfate, $BaSO_4$ (*barite*), a double carbonate of calcium and magnesium, $MgCa(CO_3)_2$ (*dolomite*). Many silicates, such as *talc*, *serpentine*, and *soapstone*, contain magnesium, and calcium phosphate is common. Magnesium chlorid, $MgCl_2$, is found crystallized with potassium chlorid, forming *carnallite*, $MgCl_2 \cdot KCl$, and magnesium sulfate, $MgSO_4$, occurs in certain mineral waters.

312. Preparation. The general method of preparing the alkalin earth metals is to electrolyze their fused chlorids. Magnesium, however, was formerly prepared by the action of metallic sodium on fused magnesium chlorid:

$$MgCl_2 + 2\,Na \rightarrow 2\,NaCl + Mg$$
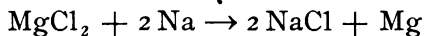
313. Properties. *Physical.* (Table I., Appendix *D.*) Magnesium is of a silvery white color, but is usually tarnished with a coat of oxid. Calcium is also silvery white, while barium and strontium have a yellowish tinge. They are all but slightly ductile and malleable.

Chemical. The alkalin earth metals remain bright in dry air, but in moist air slowly become converted into the hydroxids. When heated, they burn vigorously, magnesium emitting a most dazzling light, rich in rays affecting the photographic plate. Magnesium decomposes water only at high temperatures, while the other metals do so at ordinary temperatures. Magnesium is very soluble in most acids, setting hydrogen free, and when heated in nitrogen combines to form magnesium nitrid.

314. Uses. Metallic magnesium is used as a source of light ("flashlight") in photography. The other metals are merely chemical curiosities.

OXIDS AND HYDROXIDS

315. In General. The oxids of the alkalin earth metals are often named according to the old nomenclature, thus: MgO is *magnesia;* SrO, *strontia;* BaO, *baryta;* calcium oxid, CaO, is *quicklime.* They are all white, earth-like, almost infusible solids. They are prepared by decomposing their carbonates

or nitrates by heat. They unite with water to form hydroxids, the solubility and alkalinity of which increase with the molecular weights.

MAGNESIUM OXID, MgO. Magnesium oxid is a white, bulky powder prepared by burning magnesium or calcining its carbonate. It is known in commerce as *calcined magnesia* or *magnesia usta*.

MAGNESIUM HYDROXID, $Mg(OH)_2$. Magnesium hydroxid is ordinarily prepared by precipitating a soluble magnesium salt with either sodium hydroxid or potassium hydroxid.

316. Calcium Oxid, CaO. (*Quicklime.*) Quicklime is formed by heating to redness calcium carbonate, usually in the form of limestone or chalk.

Formerly periodic furnaces (page 114) were used. A cavity was scraped out on the side of a limestone bluff, an arch of limestone built above the fire pit, and the kiln then filled up with blocks of limestone. A fire was then lighted and kept burning for several days. At present, however, continuous furnaces are almost exclusively used for "burning" limestone.

Calcium oxid is an almost infusible solid, and because of that property it is used in the construction of electric furnaces. When exposed to the air it becomes "air-slaked," *i. e.*, it combines with the moisture and carbon dioxid to form the hydroxid and ultimately the carbonate. It unites with water with the evolution of much heat to produce calcium hydroxid, $Ca(OH)_2$, commonly called *slaked lime.*

Lime is extensively used in making mortar, cement, bleaching powder, sodium hydroxid, and glass, in purifying sugar and illuminating gas, in dyeing, in removing the hair from hides before they are tanned, and as a fertilizer and disinfectant.

317. Calcium Hydroxid, $Ca(OH)_2$. (*Slaked Lime.*) Slaked lime is a white, slightly soluble solid which, when dissolved, gives "lime water." If an excess of the finely divided solid be present, it forms a suspension popularly known as "milk of lime."

The Oxids and Hydroxids of Strontium and Barium. These closely resemble in properties and modes of preparation the corresponding compounds of calcium.

SOME IMPORTANT SALTS OF THE ALKALIN EARTH METALS

318. Magnesium Chlorid, $MgCl_2$. Magnesium chlorid is prepared by dissolving magnesium, its oxid or carbonate, in hydrochloric acid. From this solution colorless crystals are obtained, which, when heated, decompose thus:

$$MgCl_2 + H_2O \rightarrow MgO + 2\,HCl$$
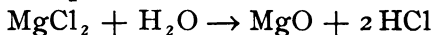
But if ammonium chlorid be added to the solution, a double chlorid, $NH_4Cl \cdot MgCl_2$, is produced which can be evaporated to dryness without decomposition. Magnesium chlorid is a deliquescent, white solid.

319. Magnesium Sulfate, $MgSO_4$. (*Epsom Salts.*) Magnesium sulfate is found in numerous springs and also in the mineral, kieserite. It forms transparent crystals of a very bitter taste. It is used in medicine, as a fertilizer, and as a dressing for cotton cloth.

320. Calcium Chlorid, $CaCl_2$. Calcium chlorid is obtained in large amounts as a by-product of several manufacturing processes. Calcium carbonate in any of its forms dissolves in hydrochloric acid, and by concentration of the solution, colorless crystals of calcium chlorid combined with six molecules of

water of crystallization are obtained. When heated, the water of crystallization passes off, leaving the salt as a porous mass, which attracts water with great eagerness, and is on that account extensively used as a drying agent for gases and liquids.

321. Calcium Fluorid, CaF_2. Calcium fluorid occurs as the mineral, *fluorspar*. It is a white, insoluble solid, and is the source of nearly all fluorin compounds.

322. Bleaching Powder or Chlorid of Lime. Bleaching powder is made by passing chlorin over freshly slaked lime. The chemical reaction as well as the formula of the product is as yet a matter of doubt. Its aqueous solution, however, behaves like a solution of calcium chlorid and calcium hypochlorite. It is a white, slightly soluble powder, that decomposes on standing. Its bleaching action is brought out more rapidly by some agent, as an acid or even certain salts, which have the power of decomposing it, and is not exercised on animal substances. In bleaching cotton or linen with it, the goods are cleansed from grease and oil, and steeped in a solution of the powder. They are then immersed in dilute sulfuric acid, whereby the chlorin is liberated and the bleaching takes place. Chlorid of lime is also a familiar disinfectant.

323. Calcium Carbonate, $CaCO_3$. Calcium carbonate occurs in immense deposits in many parts of the earth in the form of marble, limestone, chalk, and coral. The shells of molluscs and other lower forms of animals consist largely of this substance, and it is probable that the natural substances named are the remains of these animals which have, during

ages, accumulated at the bottoms of arms of the sea which have since dried up or retreated. These deposits, from pressure and elevation of temperature, have in the course of time been converted into their present forms. The original animal structure can often be detected in the hardest marble as well as in the softest chalk. Even at the present day coral reefs are in the process of formation. Calcium carbonate also occurs in two crystalline forms, arragonite and calc, or Iceland spar; the latter has the property of doubly refracting light.

DISSOCIATION OF CALCIUM CARBONATE. Calcium carbonate dissociates into carbon dioxid and lime:

$$CaCO_3 \rightleftarrows CO_2 + CaO$$
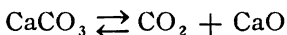
The general phenomenon of dissociation was first made clear by a study of this simple case of a solid dissociating into another solid and a gas. It was found that at every temperature above about 450° a certain definite amount of carbon dioxid was given off, which, if not allowed to escape into the air, exerted a certain definite pressure. Some corresponding values of temperature and pressure are the following :

Temperature :	547°	625°	740°	812°	865°
Pressure :	27 mm.	56 mm.	255 mm.	765 mm.	1,333 mm.

324. Limestone. Limestone is but slightly soluble in water, but its solubility is increased when carbon dioxid is present in the water. Subterranean waters not infrequently hold more or less carbon dioxid in solution, and if they flow over limestone some of the rock passes into solution and is thus carried along by the water. Caves are formed in this way. When the water loses its carbon dioxid, or evaporates, this limestone is thrown out of solution. In this way the columns found in limestone caves

have been formed. Water charged with carbon dioxid and holding limestone in solution drips from the top of the cave, evaporates somewhat, and thus loses its carbon dioxid. The calcium carbonate separates out and in the course of time forms a column projecting downwards, a *stalactite*. The water dripping to the floor loses more carbon dioxid and hence more calcium carbonate separates out and a corresponding column is built up, a *stalagmite*. Stalactite and stalagmite may ultimatelv meet and form a continuous column.

325. Calcium Sulfate, $CaSO_4$. Calcium sulfate is very abundant in nature; the chief natural variety is gypsum, which is used in making plaster of Paris and land plaster, a fertilizer. Alabaster is a granular form of gypsum.

326. Plaster of Paris. Plaster of Paris is prepared by heating gypsum to a little over 100°, so as to expel most of its water of crystallization. When mixed with water, it takes up its water of crystallization and the result is a white, rather hard mass; the plaster " sets." As this process is accompanied with an expansion the setting plaster makes a sharp cast, and it is widely used for this purpose. Mixed with lime it forms the " hard finish " or " putty coat." If heated above 200°, gypsum loses this property of recombining with its water of crystallization and is valueless for making plaster casts.

327. "Hard Water." Most spring and well waters will not at once form a lather with soap, but become filled with curd-like material when mixed with a soap solution. Such waters are said to be "hard." Certain of these natural waters have most

18

of their hardness removed by boiling, and they are found to hold calcium carbonate in solution. Other waters, however, do not lose their hardness when boiled, and it is found that they contain calcium sulfate. The addition of sodium carbonate to such hard waters precipitates the alkalin earth carbonates, and thus "softens" the water. Water containing only calcium carbonate is said to be "temporarily hard," while if the sulfate of calcium be present, it is said to be "permanently hard."

CALCIUM SULFID, CaS. Calcium sulfid is produced by reducing calcium sulfate with carbon at high temperatures:

$$CaSO_4 + 4\,C \rightarrow CaS + 4\,CO$$
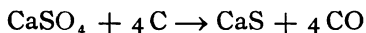
or by passing hydrogen sulfid over hot slaked lime:

$$Ca(OH)_2 + H_2S \rightarrow CaS + 2\,H_2O$$
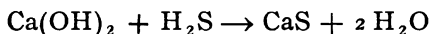
Calcium sulfid is a white, insoluble powder which, after exposure to light, becomes self-luminous in the dark. Hence it is used in making luminous paint.

328. Calcium Phosphate, $Ca_3(PO_4)_2$. Calcium phosphate occurs in nature as the mineral phosphorite, and may be prepared by adding sodium phosphate to a solution of calcium chlorid containing some ammonia. It is the main constituent of the ashes of bones. It reacts with nitric and hydrochloric acids to form soluble compounds, and when treated with sulfuric acid is decomposed, thus:

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \rightarrow 2\,CaSO_4 + CaH_4(PO_4)_2$$
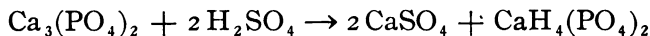
The mixture of calcium sulfate and mono-calcium phosphate thus obtained is extensively used as a fertilizer under the name of "superphosphate of lime."

329. The Nitrates of the Alkalin Earth Metals.
The nitrates of the alkalin earth metals are prepared by dissolving their carbonates or oxids in dilute nitric acid. They are all white, soluble solids. When strontium nitrate, $Sr(NO_3)_2$, is heated with carbon or other easily combustible substances, the mixture burns with a red flame. Barium nitrate, $Ba(NO_3)_2$, under similar conditions, gives a green flame. These mixtures are, on this account, used in the manufacture of fireworks.

330. Barium Sulfate, $BaSO_4$. Barium sulfate occurs in nature, forming large crystals with a high specific gravity, and on that account it is known as heavy spar or barytes. It is formed as a dense, white precipitate when a solution of barium salt is mixed with sulfuric acid. It is used as a paint under the name of " permanent white."

Exercises

1. How is magnesium utilized in separating argon from air?

2. What class of substances is formed by the action of water on the products of combustion of the alkali and alkalin earth metals?

3. By what chemical tests would you distinguish marble from fluorspar?

4. What objections are there to the use of hard water in a steam engine and in a laundry?

5. Devise tests for ascertaining the composition of the foundation stone of your school building.

6. If the cost of magnesia and lime is the same, which is the more economical for liberating ammonia from its salts?

Problems

1. How many grams of calcium oxid can be obtained from $1.5^{kg.}$ of marble?

2. What is the percentage composition of crystallized barium chlorid, $BaCl_2 + 2 H_2O$?

3. How much $BaCl_2 + 2 H_2O$ is required to precipitate exactly as $BaSO_4$ the sulfuric acid in 10^g of $Na_2SO_4 + 10 H_2O$?

4. Dumas, in 1859, found as the result of sixteen determinations that 61.6407^g of barium chlorid gave precipitates with silver nitrate containing 63.9964^g of silver. If the atomic weights of chlorin and silver are 35.45 and 107.94, respectively, what is the atomic weight of barium?

5. Heinrichson, in 1902, heated 31.20762^g of calcite and obtained 17.49526^g of quicklime. If the atomic weights of oxygen and carbon are 16.000 and 12.001, respectively, what is the atomic weight of calcium?

6. Richards, in 1902, found that 9.00246^g of calcium chlorid, when mixed with a solution of silver nitrate, yielded 23.2506^g of silver chlorid. If the atomic weights of silver and chlorin are 107.94 and 35.45, respectively, what is the atomic weight of calcium?

7. Marignac, in 1884, converted 16.0263^g of magnesium oxid into 47.8015^g of magnesium sulfate. Taking the atomic weights of oxygen and sulfur as 16.00 and 32.06, respectively, calculate the atomic weight of magnesium.

The same chemist also obtained from 59.4763^g of magnesium sulfate, 19.9379^g of magnesia. Calculate from these data the atomic weight of magnesium.

8. Scheerer, in 1846, obtained 3.8855^g of barium sulfate by adding a solution of barium salt to a solution containing 2.0065^g of magnesium sulfate. Assuming the atomic weights of oxygen, sulfur, and barium to be 16.00, 32.06, and 137.04, calculate the atomic weight of magnesium.

9. 25^g of magnesite, $MgCO_3$, were dissolved in dilute sulfuric acid and the solution slowly evaporated at 20°. After 10^g of magnesium sulfate had crystallized, how much water was in the mother liquor, the solubility of magnesium sulfate at 20° being 20 per cent?

10. Stromeyer, in 1816, on dissolving 0.5^g of strontium carbonate in acid obtained $75.54^{c.c.}$ of carbon dioxid at 0° and 760^{mm}. Taking the weight of one liter of the gas as equal to 1.966^g and the atomic weights of oxygen and carbon as 16.00 and 12.00, respectively, calculate the atomic weight of strontium.

BORON AND SILICON

Boron and silicon resemble carbon in their physical properties; their compounds, however, are widely different.

BORON

331. Occurrence. Boron never occurs free; its principal compounds are boric acid, H_3BO_3, and borax, $Na_2B_4O_7$; the former is found in Tuscany, the latter in Tibet, California, and Nevada.

332. Preparation. The reduction of boron trioxid, B_2O_3, at a high temperature, by means of potassium, sodium, magnesium, or aluminum, yields the element in the form of an amorphous brown powder.

333. Properties. Amorphous boron dissolves in molten aluminum and on cooling separates into crystals, sometimes transparent, but usually brown in color. This crystalline variety, which always contains some carbon and aluminum, closely resembles the diamond in hardness, refractive power, and luster. Boron at a red heat combines directly with nitrogen, forming boron nitrid, BN, a light powder, white in color and very stable. Boron burns to boron trioxid, B_2O_3.

334. Boric Acid. (*Boracic Acid.*) In certain volcanic districts in Tuscany, jets of steam, containing boric acid in small amounts, issue from the ground

These jets of steam are made to pass into tanks of water, which, as the water evaporates, become filled with crystals of boric acid. This has a glassy appearance and a soapy feel. When heated to about 100° it loses water and is converted into *metaboric acid*, HBO_2:

$$H_3BO_3 - H_2O \rightarrow HBO_2$$
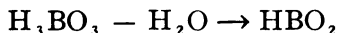
At a higher temperature, metaboric acid loses water, and *tetraboric acid*, $H_2B_4O_7$, is produced:

$$4HBO_2 - H_2O \rightarrow H_2B_4O_7$$
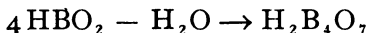
And at a higher temperature still, boron trioxid is formed:

$$H_2B_4O_7 - H_2O \rightarrow 2B_2O_3$$
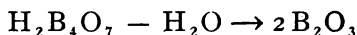
If a solution of boric acid in alcohol be ignited, the flame is tinged green from the volatile acid.

Boric acid is used in the manufacture of enamels and glazes for pottery, for preserving meat, and as an antiseptic.

335. Borax. When solutions of boric acid and sodium carbonate are heated together, carbon dioxid is evolved and borax (*sodium tetraborate*) is formed:

$$4H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + CO_2 + 6H_2O$$
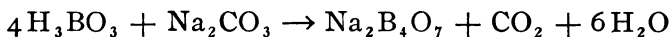
Borax is found native in the beds of dried-up lakes. It has an alkalin taste and reaction, and usually crystallizes with ten molecules of water. When heated it swells up at first into a white porous mass from loss of water of crystallization, and finally melts to a clear, glassy liquid which has the property of dissolving many metallic compounds. As these ofttimes impart a characteristic color to it, this behavior is applied as a test for certain metals in chemical analysis; the usual

procedure is to melt borax in a loop of platinum wire so as to form a transparent globule, and to add a little of the compound to be tested to the bead. The colors which the beads may assume depend upon the metal in the tested compound, and also as to whether it is heated in the oxidizing or reducing flame of a blowpipe. Acids take the sodium from borax in solution, so that boric acid is formed.

Borax is used in the manufacture of soap, glass, varnish, and artificial gems; also in medicine and in the laundry.

SILICON

Just as carbon is the central element in the animal and vegetable kingdoms, so is this very similar element central in the mineral kingdom. Silicon compounds are very numerous and widespread, and silicon is, next to oxygen, the most abundant element known.

336. Occurrence. Silicon is never found free. Its compounds, however, are almost omnipresent; hundreds of minerals and rocks are composed of *silicates*.

337. Preparation. Silicon is obtained when potassium fluosilicate, K_2SiF_6, is heated with sodium or potassium:

$$K_2SiF_6 + 4K \rightarrow 6KF + Si$$
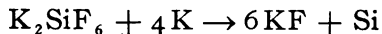
The potassium fluorid, KF, is washed out, leaving the silicon as an amorphous, brown powder. The crystalline variety may be obtained by adding zinc or aluminum to the original mixture so that the silicon may crystallize out of the molten metal. It is also obtained by reducing silicon dioxid, SiO_2,

with carbon, magnesium, or aluminum in an electric furnace.

338. Properties. Silicon, like carbon, presents three allotropic modifications, amorphous, graphitoidal, and crystalline. All three forms are quite stable and not affected by the action of the usual reagents.

339. Silicon Dioxid. (*Silica.*) Silicon, unlike carbon, forms but one oxid, SiO_2, which is one of the most abundant and important of substances. *Quartz, chalcedony, jasper, opal, sandstone,* and *sand* are nearly pure silica. It enters into the composition of several rocks, and is found in the stems of many rushes and grasses. *Diatomaceous* or *infusorial earth* is mainly silica consisting of the shells of microscopic organisms called diatoms. Silica melts only at a very high temperature and is insoluble in pure water.

340. Quartz. Quartz makes up nearly a third of the weight of the rocks occurring in the earth's crust. It usually crystallizes in hard six-sided prisms, terminated by six-sided pyramids. Quartz containing only silica is as transparent as glass, and is fashioned into gems known as "white stones" and into "pebble" lenses for spectacles and optical instruments. It is also melted in an oxyhydrogen flame, and blown into beakers, flasks, and other articles for use in chemical laboratories. Such "quartz ware" is very refractory to heat, and stands sudden changes of temperature without cracking. Colored violet with a little manganese dioxid, it forms the highly prized gem, *amethyst. False topaz* is quartz colored yellow, and *smoky quartz* varies in color from nearly white to quite black.

341. Amorphous Silica. Alkalin waters dissolve not inconsiderable amounts of silica, especially under pressure at high temperatures. The mouths of geysers have been built up of the silica deposited by the alkalin water released from pressure and cooled on escaping into the air. Agate, chalcedony, and opal have also been deposited from solution. Wood decaying under water holding silica in solution has its particles replaced by silica, so that in course of time the wood turns into stone, *i. e.*, petrifies; the structure of the wood is perfectly copied. Silica is insoluble in all acids except hydrofluoric. When fused with alkalin hydroxids or carbonates, it forms the silicates used in glass-making.

Sandstone is an important building stone and some especially hard and fine-grained varieties are made into whetstones and grindstones. Sand is used in making mortar, glass, porcelain, and sandpaper. Infusorial earth is used to polish silver (a common commercial article is "electro-silicon"), and in making dynamite, some cements, and refractory brick.

342. Silicon Hydrid, SiH_4. Silicon hydrid is a colorless gas obtained by the action of hydrochloric acid on magnesium silicid, $SiMg_2$. As thus prepared, silicon hydrid is spontaneously inflammable, but when purified, it has to be heated before it will take fire.

343. Silicon Tetrachlorid, $SiCl_4$. Silicon tetrachlorid is made by passing chlorin over a mixture of silica and charcoal heated to a white heat. It is a volatile, colorless liquid, totally decomposed by water (§ 346).

344. Silicon Tetrafluorid, SiF_4. Silicon tetra-fluorid is a gas formed by the action of hydrofluoric acid on silicon and its compounds. It reacts with water very vigorously, but is only partially decomposed, as the reaction is reversible.

345. Carborundum. Carborundum is carbon silicid, CSi, and is formed by heating to a very high temperature in an electric furnace a mixture of carbon, sand, and salt. The salt reacts with the metallic impurities, converting them into chlorids which escape in the form of vapor. The silicon dioxid is reduced and combines with the excess of carbon present to form carborundum.

Carborundum is almost as hard as the diamond, and is extensively used for grinding and polishing purposes; it is mixed with a "body" of clay and feldspar, molded into the desired shapes, such as wheels and hones, and heated to a temperature high enough for the mixture to become vitrified, *i. e.*, converted into a strongly coherent mass.

346. Silicic Acids. Silicon chlorid reacts with water thus:

$$SiCl_4 + 4\,H_2O \rightarrow Si(OH)_4 + 4\,HCl$$
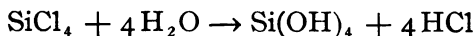
The normal silicic acid thus formed easily loses water to form ordinary silicic acid, H_2SiO_3, and when heated, this loses water and is converted into silica, SiO_2. Most of the ordinary silicates are derived from the acid of the formula, H_2SiO_3. Thus, when an alkalin carbonate is fused with sand, the silicate formed corresponds to a salt derived from an acid of the formula, H_2SiO_3. For example:

$$SiO_2 + K_2CO_3 \rightarrow K_2SiO_3 + CO_2$$
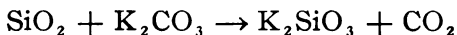
Potassium (and also sodium) silicate is soluble in water and, if hydrochloric acid is added to a solution of such a silicate, the gelatinous precipitate formed is probably mainly silicic acid, H_2SiO_3. Besides these there are many other silicic acids of more complex composition, which may be regarded as derived from two or more molecules of the simpler ones by the abstraction of water:

$$2\,H_2SiO_3 - H_2O \rightarrow H_2Si_2O_5$$
$$3\,H_2SiO_3 - H_2O \rightarrow H_4Si_3O_8, \text{ etc.}$$
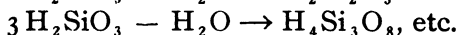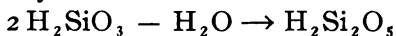
Some of these *polysilicic acids* occur in nature; *opal* is an example. Ordinary silicic acid is obtained by adding dilute hydrochloric acid to a solution of an alkalin silicate; it presents the appearance of a white gelatinous mass.

SILICATES. Silicates in endless variety are found in nature. Many important minerals and rocks are silicates, as feldspar and mica, which, together with quartz, form granite. Slate, clay, and soapstone are silicates. Only silicates of the alkali metals are soluble in water.

GLASS

347. Properties of Glass. When a mixture of sand, limestone, and carbonate of soda is strongly heated, it fuses to a clear transparent liquid which on cooling does not solidify at a certain definite temperature, but remains pasty throughout a considerable range of temperature. When in this state it may be given any desired shape which is retained when it becomes cold and solid. It is to this property and to its transparency that glass owes its value.

MANUFACTURE. The mixture destined for the preparation of the glass is placed in fire-clay pots and heated in a circular furnace. As the temperature rises the

mass fuses and gives off carbon dioxid, finally becoming quite fluid. The workman takes out the glass and either blows or molds it into the desired shape. After this is done the objects are put into an annealing furnace and are allowed to cool very gradually. Annealing is absolutely necessary, as the glass is otherwise brittle.

Glass, chemically considered, is an amorphous mixture of the silicates of alkalin and alkalin earth metals, although other metals may also be present. The properties of the glass depend upon the nature of its ingredients as well as their proportion. Sodium makes glass brilliant and fusible, but gives it a greenish tinge. Potassium imparts no color, but renders the glass less brilliant and fusible. Calcium increases its hardness and luster, but diminishes its fusibility, while lead diminishes its hardness and gives heaviness and luster.

WINDOW GLASS. Window glass is made from white sand, chalk or slaked lime, and soda-ash (sodium carbonate) or salt-cake (sodium sulfate); broken glass, called *cullet*, is added to make the mixture fuse more readily. This glass is therefore a mixture of the silicates of sodium and calcium.

BOTTLE GLASS. Bottle glass is made like window glass, but the materials are not so pure. It usually contains some iron, which imparts to it a green color.

FLINT GLASS. Flint glass — so called because powdered flint, a kind of amorphous silica, was formerly used in manufacturing it—is a mixture of potassium and lead silicates. It is comparatively soft and heavy, and has so high a refracting power as to be very brilliant. Under the name of "crystal" it is used in making the best grades of lenses and table glassware. It fuses more readily than other kinds of glass, and does not resist the action of chemicals well enough to be used in the laboratory. If it contains as much as 50 per cent of lead, the glass is called "paste" and is used in making imitation gems.

BOHEMIAN GLASS. Bohemian glass is a mixture of potassium and calcium silicates. It is hard, melts with difficulty, and is but slightly affected by chemicals. Hence it is well suited for chemical glassware.

COLORING GLASS. Glass is colored by the addition of certain metallic oxids. Thus, cobalt oxid gives a dark blue color, manganese dioxid a violet, uranium oxid a yellow, gold oxid a ruby red, chromium oxid a green. White enamel is glass rendered white and opaque by tin or antimony oxid.

PAINTING ON GLASS. Painting on glass is done by pigments made of various inorganic substances ground up with a very fusible glass and turpentine. After the colors have dried, sufficient heat is applied to just melt the more fusible glass.

348. Mortar. Mortar is made by mixing slaked lime (calcium hydroxid), $Ca(OH)_2$, with sharp sand and water; if hair be added, the product is *plastering*. The hardening of the mortar is an imperfectly understood process. The slaked lime combines with the carbon dioxid of the air to form calcium carbonate. The sand serves mainly to make the mass porous so that the air (and the CO_2 in it) may penetrate into the mortar. The hardening is a slow process, and the older the mortar the harder it is and the better it cements the bricks and stones together.

349. Hydraulic Cements or Mortars. Hydraulic cements contain clay and a larger proportion of sand than ordinary mortar. They harden even under water. Portland cement is made by heating three parts of lime to one of clay until water and carbon dioxid have been expelled, and then pulverizing the mixture. With water and sand it forms a stony mass which becomes harder, stronger, and more durable than many natural building stones.

Exercises

1. How can you determine whether a given crystal is quartz or calcspar?

2. What class of substances must be present in subterranean waters so that silica may be held in solution? What substance is required to keep calcium carbonate in solution? Can a natural water hold in solution at the same time silica and calcium carbonate? Why?

3. What are the products obtained by heating sodium sulfate with boracic acid?

4. The products of the combustion of silicon hydrid are silica and water. Write the balanced equation for the reaction.

5. Compare the properties of the hydrogen and oxygen compounds of silicon with the corresponding compounds of carbon.

Problems

1. What is the percentage composition of (*a*) quartz, (*b*) borax?

2. How many grams of carbon dioxid are evolved when 100 g. of borax are made by the interaction of boric acid and washing soda?

3. Which contains the larger percentage of boron, boric acid or boron trioxid?

4. Pelouze, in 1845, found that the chlorin in 2.621 g. of silicon tetrachlorid, $SiCl_4$, united with 6.6445 g. of silver. If the atomic weight of silver is 107.94, calculate that of silicon.

5. Thorpe and Young, in 1887, decomposed 95.52367 g. of silicon tetrabromid, $SiBr_4$, by action with water, and obtained 16.56868 g. of silica. If the atomic weights of oxygen and bromin are 16.00 and 79.96, respectively, find the atomic weight of silicon.

CHAPTER XXV

ZINC, CADMIUM, AND MERCURY

ZINC

350. Occurrence. Zinc is found only in combination; its principal natural compounds are the carbonate, $ZnCO_3$ (*smithsonite*), the silicate, $H_2Zn_2SiO_5$ (*calamine*), the sulfid, ZnS (*sphalerite* or *zinc blende*), and red zinc oxid, ZnO (*zincite*).

351. Metallurgy. The zinc ores are converted into zinc oxid by roasting, *i. e.*, heating with free access of air, and subsequent reduction with charcoal.

$$ZnCO_3 \rightarrow ZnO + CO_2$$
$$2\,ZnS + 3\,O_2 \rightarrow 2\,ZnO + 2\,SO_2$$
$$ZnO + C \rightarrow Zn + CO$$
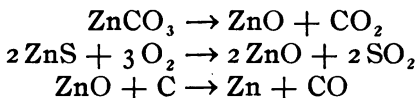
The zinc vaporizes and then at first condenses into a powder ("zinc dust"), but finally into a liquid which is drawn off and cast in bars called *spelter*. It contains other metals and is refined by distilling it in earthenware retorts.

352. Properties. *Physical.* (Table I., Appendix *D*.) Zinc has a bluish-white color and high luster. At ordinary temperatures it is rather brittle; when heated to 100 to 150° it becomes so malleable that it can be rolled into sheets, while above 200° it is brittle enough to be powdered.

Chemical. Zinc is inalterable in dry air at ordinary temperatures, but in moist air becomes coated with a thin covering of the oxid. When heated to

a sufficiently high temperature, it burns with a bluish flame. Pure zinc is but slowly attacked by acids, but the commercial form dissolves readily both in acids and in alkalis.

VAPOR DENSITY OF ZINC: A liter of zinc vapor weighs 30.4$^{g.}$, *i. e.*, it is 33.8 times as heavy as a liter of hydrogen. As its specific heat shows that its atomic weight is 65.4, it follows that the molecule of vaporized zinc contains but one atom. The same is true of cadmium and mercury.

353. Uses. Zinc is extensively used in electric batteries, in gutters, bath tubs, and to protect woodwork from the heat of a stove. Iron dipped into molten zinc becomes covered with a coating of the latter metal, which protects it against the action of the weather; this is known as "galvanized iron" and is extensively used for roofs, pipes, cornices, and tanks. Zinc is a constituent of the alloys, *brass* (copper and zinc), *German silver* (copper, zinc, and nickel), and *bronze* (copper, tin, and zinc).

SOME IMPORTANT COMPOUNDS OF ZINC

354. Zinc Oxid, ZnO. Zinc oxid is obtained by burning zinc or by heating its carbonate or nitrate. Familiar names for it are "flowers of zinc" and "philosopher's wool." When hot it has a yellow color; when cold, white. It is employed as a paint under the name of *zinc white*.

355. Zinc Chlorid, $ZnCl_2$. Zinc chlorid may be obtained by dissolving zinc in hydrochloric acid or distilling a mixture of zinc sulfate and sodium chlorid:

$$ZnSO_4 + 2\,NaCl \rightarrow Na_2SO_4 + ZnCl_2$$
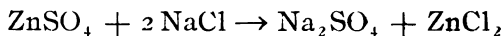
Zinc chlorid is a white, translucent substance, melting easily and distilling at a red heat. It dissolves in both water and alcohol, and is very deliquescent. It is used in medicine and in soldering. Wood impregnated with it is preserved from decay.

NOTE. The "cut acid" of the plumber is zinc chlorid, prepared by dissolving zinc in muriatic (hydrochloric) acid.

356. Zinc Sulfate, $ZnSO_4$. Zinc sulfate much resembles magnesium sulfate. It is prepared by roasting zinc sulfid or by dissolving zinc in sulfuric acid. It is a white, efflorescent salt, used in medicine and in dyeing.

ZINC SULFID, ZnS. Zinc sulfid separates as a white precipitate when an alkalin sulfid is added to a solution of a zinc salt.

CADMIUM

357. Occurrence and Properties. Cadmium is ordinarily found associated with zinc, and is a white, lustrous metal tarnishing in moist air. At temperatures somewhat above its melting point (315°) it takes fire and burns with a brownish flame to cadmium oxid, CdO. It is soft enough to be cut with a knife, and is quite ductile and malleable. It is an important constituent of the amalgams used by dentists for filling teeth.

CADMIUM SULFID, CdS. Cadmium sulfid is precipitated as a bright yellow solid when hydrogen sulfid is passed into a solution of a cadmium salt; it is used as a paint.

MERCURY

358. Occurrence. Mercury sometimes occurs free in little globules in certain rocks, but is principally obtained from its sulfur ore, *cinnabar*, HgS.

359. Preparation. Cinnabar is roasted, whereby mercury and sulfur dioxid are formed; the sulfur dioxid passes off and the mercury is collected in a series of condensing chambers, filtered through cloth, and distilled.

360. Properties. (Table I., Appendix *D*.) Mercury is the only one of the metals which is liquid at ordinary temperatures. It is silvery white, with a brilliant luster. It does not change in the air unless heated to its boiling point (360°), when it oxidizes to mercuric oxid, HgO. It is insoluble in hydrochloric acid and cold sulfuric acid. It reduces hot sulfuric acid and dissolves in nitric acid. With most metals it forms alloys, called *amalgams;* iron and platinum are notable exceptions.

361. Uses. Mercury is extensively used in making thermometers and barometers, in amalgamating the zinc plates of electrical batteries, and in the extraction of gold and silver from their ores. A tin amalgam is employed in the manufacture of mirrors.

SOME IMPORTANT COMPOUNDS OF MERCURY

362. Salts. Mercury forms two series of salts. In mercurous salts, it is univalent; in mercuric, bivalent.

363. Mercuric Oxid, HgO. Mercuric oxid, which is also called *red oxid of mercury* and *red precipitate*, forms when mercury is heated to its boiling point. It is black when hot, and either red and crystalline or yellow and amorphous when cold. At high temperatures it breaks up into oxygen and mercury (§ 30).

364. Mercuric Chlorid, $HgCl_2$. (*Corrosive Sublimate.*) Corrosive sublimate is made by subliming an intimate mixture of mercuric sulfate and common salt:

$$HgSO_4 + 2\,NaCl \rightarrow Na_2SO_4 + HgCl_2$$
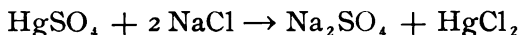
It is a white, crystalline solid, soluble in water. It is very poisonous and is used as an antiseptic.

365. Mercurous Chlorid, $HgCl$. (*Calomel.*) Calomel is manufactured by subliming an intimate mixture of mercuric chlorid and mercury:

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2 \text{ or } 2\,HgCl$$

It is also formed when any soluble chlorid is added to a solution of a mercurous salt. It is a heavy, white solid, insoluble in water. It is used extensively in medicine.

366. Mercuric Sulfid, HgS. Mercuric sulfid occurs in Spain, Austria, and California as the mineral, *cinnabar*. It is the most important ore of mercury and furnishes the greater part of mercury used. It may be prepared by rubbing flowers of sulfur together with mercury or by passing hydrogen sulfid into a solution of a mercury salt, when it is thrown down as a black powder which turns red when sublimed. It is used as a pigment under the name of *vermillion*.

367. Mercury Nitrates. *Mercurous Nitrate*, $HgNO_3$, results from the action of nitric acid on an *excess* of mercury at ordinary temperatures, while *mercuric nitrate*, $Hg(NO_3)_2$, is formed when the acid is in excess and the reaction is made to take place at a higher temperature. They are both white, crystalline solids.

Exercises

1. How is the zinc used in the extraction of silver from lead "recovered" so that it may be used over and over again?

2. Under what circumstances are paints made from "zinc white" preferable to white-lead paints?

3. Suppose a deposit of an ore was found, an analysis of which showed it to be mercury oxid mixed with some sand and light earthy materials. What metallurgical process would you suggest for obtaining the mercury in a pure state?

4. What are the properties of mercury that make it adapted for use in (*a*) thermometers, (*b*) barometers?

5. What physical properties of mercury does its common name, "quicksilver," connote?

Problems

1. What is the specific heat of cadmium if its atomic weight is 112?

2. How much (*a*) corrosive sublimate, (*b*) calomel can be obtained from 100 $g.$ of mercurous sulfate?

3. What is the percentage composition of zinc silicate, Zn_2SiO_4?

4. Van der Plaats, in 1885, dissolved 29.6754 $g.$ of zinc in dilute sulfuric acid and obtained 5.0834 $l.$ of hydrogen. What is the equivalent weight of zinc? The atomic weight?

5. 50 $g.$ of zinc were dissolved in dilute sulfuric acid and the solution allowed to evaporate slowly at 10°. If the solubility of zinc sulfate at 10° is 30 per cent, how much water was present in the mother liquor when 20 $g.$ of the salt had crystallized out?

6. Hauer, in 1858, found by heating 64.2051 $g.$ of cadmium sulfate, $CdSO_4$, that 44.4491 $g.$ of cadmium sulfid were left. Taking the atomic weights of oxygen and sulfur as 16.00 and 32.06, respectively, calculate the atomic weight of cadmium.

7. Huntington, in 1882, added silver nitrate to a solution of cadmium bromid, $CdBr_2$, and found the ratio of the weights of cadmium bromid taken and silver bromid formed to be 23.3275 : 32.2098. The atomic weights of silver and bromin are 107.94 and 79.96, respectively; calculate the atomic weight of cadmium.

8. How much sulfuric acid could theoretically be obtained from 1,000 $kg.$ of cinnabar, HgS?

9. Morse and Burton, in 1888, oxidized 16.03161 g. of zinc with nitric acid, obtaining 20.2608 g. of zinc oxid. Calculate the atomic weight of zinc.

10. How many kilograms of mercury can be obtained from 50 kg. of cinnabar by heating in a furnace whereby the sulfur burns to sulfur dioxid, and the mercury vaporizes and is afterward condensed?

11. Erdmann and Marchand, in 1844, obtained 352.4079 g. of mercury by heating 380.5744 g. of mercuric oxid. What is the atomic weight of mercury?

12. Millon, in 1846, found that corrosive sublimate contained 73.845 per cent of mercury. The atomic weight of chlorin is 35.45; what is that of mercury?

13. How many liters of oxygen at 20° and 743 mm. can be obtained from 50 g. of mercuric oxid?

14. Erdmann and Marchand, in 1844, heated 177.1664 g. of mercuric sulfid and obtained 152.7450 g. of mercury. The atomic weight of sulfur is 32.06; what is that of mercury?

CHAPTER XXVI

ALUMINUM

368. Occurrence. Aluminum does not occur free in nature, but in combination is found in large quantities and very widely diffused. Its most common and plentiful compounds contain oxygen and silicon. *Feldspar*, $KAlSi_3O_8$, is a silicate of potassium and aluminum. *Mica* is a general name applied to mineral silicates of aluminum, potassium, and magnesium. *Bauxite* is a mixture of the hydroxids of aluminum and iron. *Cryolite* is a fluorid of aluminum and sodium. Pure *clay* or *kaolin* is a hydrated orthosilicate of aluminum, $Al_4(SiO_4)_3 + 4 H_2O$, and is white; the different colors of ordinary clay are due to the presence of other compounds, those of iron predominating.

369. Metallurgy. Aluminum was first prepared by the action of sodium on aluminum chlorid, $AlCl_3$. Electrolytic methods, however, have superseded this method. Of these, several have been proposed, but the most successful is known as the "Hall's Process." Iron tanks are lined with carbon, forming the cathode, while large carbon rods form the anode. The electrolyte is aluminum oxid dissolved in a melted mixture (*flux*) of cryolite. The mixture is melted and kept in fusion by the great heat evolved because of the high resistance to the

passage of the electric current (Fig. 36). The aluminum collects in liquid form at the bottom of the tanks, while the oxygen combines with the carbon to form carbon monoxid. As the aluminum oxid becomes electrolyzed, more is put into the flux from time to time. The cryolite itself, acting merely as a solvent, undergoes no change.
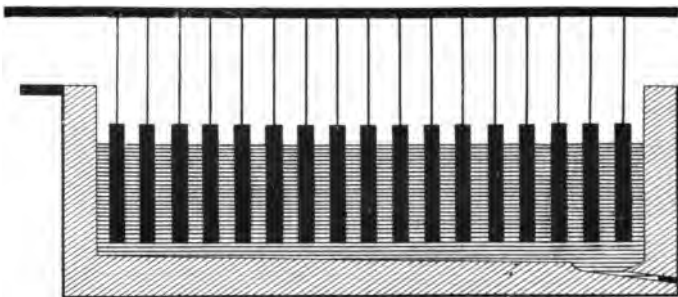
Fig. 36 — THE ELECTRIC FURNACE USED IN PREPARING ALUMINUM BY 'HALL'S PROCESS"

370. Properties. *Physical.* (Table I., Appendix *D*.) Aluminum is a silvery white metal of about the same density as glass. It is very strong, quite malleable, but not very ductile. It does not "work" well in a lathe and is hard to weld or solder. It is a good conductor of heat and electricity, and is a serious competitor of copper in electric conductors.

Chemical. Aluminum is not affected appreciably by moist or dry air, even when carbon dioxid, hydrogen sulfid, or other corrosive gases are present. It is hardly attacked by nitric acid, and is dissolved but slowly by sulfuric acid. Hydrochloric acid and the fixed alkalis dissolve it readily.

THERMOLYSIS. Aluminum reduces many oxids with evolution of great heat. This property is utilized in the

preparation of certain metals and is also being applied in the welding of steel rails. The ends of the rails are brought together and covered with a mixture of iron oxid, sand, and aluminum powder, together with a cement to make the mixture compact. A "primer," consisting of a mixture of substances rich in oxygen, as potassium chlorate, etc., and a piece of magnesium ribbon, is placed in the above mixture and the ribbon ignited with a match. The reaction then spreads through the entire mass, producing heat enough to weld the rails together.

371. Uses and Alloys. Aluminum is coming more and more into general use in the form of kitchen utensils, small wares, surgical and scientific instruments. Aluminum leaf is used to decorate book covers and signs, and aluminum powder is applied in painting many metallic objects, such as letter boxes and radiators, which are exposed to heat or to the weather. It forms many valuable alloys. Less than one per cent added to steel greatly improves it. *Aluminum bronze*, an alloy of copper and aluminum, resembles gold in appearance and is very strong and non-corrosive. *Magnalium* is an alloy of aluminum and magnesium.

SOME IMPORTANT COMPOUNDS OF ALUMINUM

372. Salts. Aluminum is always trivalent, and forms no salts with very weak acids.

SOURCE OF COMPOUNDS. Aluminum compounds were formerly prepared from *alum shale*, a mixture mainly of the silicates of aluminum and potassium and of iron sulfid. This is broken up into small pieces, heaped up with coal or wood, which is set on fire and allowed to smolder for some time. The product is then spread out and exposed to the weather for some months. The sulfur combined with the iron is oxidized to sulfuric acid,

which decomposes the silicates. The final products are chiefly the sulfates of potassium, aluminum, and iron. These are leached out and allowed to crystallize; the aluminum and potassium sulfates separate out first as alum.

The chief sources of aluminum compounds nowadays are bauxite and cryolite. When bauxite is heated with sulfuric acid, a mixture of aluminum and iron sulfates is obtained, which is known as "alum cake," and is extensively used in purifying water (page 41). When bauxite is heated with soda ash soluble sodium aluminate is formed, the solution of which, when separated from the insoluble impurities and treated with carbon dioxid gas, gives a precipitate of fairly pure aluminum hydroxid. The sulfuric acid converts this into the sulfate; the product is known as "concentrated alum." Cryolite also, when boiled in milk of lime, forms sodium aluminate, from which "concentrated alum" may be obtained.

373. Alums. Alums are double sulfates of a trivalent metal, such as aluminum, and an univalent metal, such as potassium, which always crystallize with twenty-four molecules of water. The formula of ordinary or potash alum is $Al_2(SO_4)_3 \cdot K_2SO_4 + 24 H_2O$. All alums are soluble in water and have a more or less pronounced astringent taste. Sodium alum, $Al_2(SO_4)_3 \cdot NaSO_4 + 24 H_2O$, is used in the manufacture of some baking powders. Potash alum is used in dyeing and printing cloth, in tanning and paper making, in purifying water, in making wood and cloth fireproof, and as a medicine.

374. Aluminum Hydroxid, $Al(OH)_3$. Aluminum hydroxid is precipitated as a white, gelatinous mass when ammonia is added to a solution of any aluminum salts. It is soluble in acids, forming the corresponding salts. It is also soluble in the fixed alkalis, forming salts called *aluminates*, in which the

hydrogen of the hydroxyl is replaced by alkali metal, as shown in the formulas for potassium and sodium aluminates, $Al(OK)_3$ and $Al(ONa)_3$. When aluminum hydroxid is heated it loses water, and a compound of the formula, $HAlO_3$, is formed. This acts as an acid and forms salts, some of which are minerals, as *spinel*, which is magnesium aluminate, $Mg(AlO_2)_2$. When heated to a still higher temperature, aluminum hydroxid is converted into aluminum oxid.

375. Aluminum Oxid, Al_2O_3 (*alumina*). Aluminum oxid is a white powder insoluble in water. It occurs in nature as *corundum*, which is nearly as hard as diamond. An impure variety is *emery*, much used in grinding and polishing. The *ruby* is crystallized alumina colored with chromium oxid, while the sapphire is colored with cobalt.

The ruby and the sapphire can be prepared artificially by heating aluminum oxid with lead oxid in a Hessian crucible to a bright red heat ; a little potassium dichromate or cobalt chlorid is added to give the characteristic color of the ruby or sapphire, respectively. The silica of the crucible acting on the compound of lead oxid and alumina formed sets free the alumina in crystals closely resembling the natural gems.

ALUM TANNING. When water-soaked hides are placed in a solution of potash alum containing common salt, alumina is deposited in the fibers of the skin and serves to prevent hardening. The skin is then thoroughly rubbed and worked with fat, yielding a strong and pliable leather. Leather for kid gloves is made in this way from the skins of lambs and kids.

MORDANTS. In dyeing cloth, especially cotton, it is often necessary to employ a mordant to fix the color and make it fast. The cloth is first saturated with the mordant and, when dry, is dipped into a solution of the coloring matter. This reacts with the mordant, with

the result that the solid color is precipitated right in the fiber and cannot be removed by washing. Aluminum acetate and sulfate, as well as alum, are much used as mordants.

376. Aluminum Chlorid, $AlCl_3$. Aluminum chlorid is formed by the action of hydrogen chlorid on aluminum filings heated in a porcelain or glass tube. The white powder sublimes from the heated tube into the receiver. It is extremely hygroscopic and its aqueous solution hydrolyzes so readily that it can be preserved only by the addition of an excess of hydrochloric acid. On evaporation the hydroxid is the only non-volatile product, as the hydrochloric acid continually escapes so that more of the chlorid is dissociated in order to maintain the equilibrium.

ALUMINUM CARBONATE AND SULFATE. When solutions of aluminum salts are mixed with a solution of a carbonate or a sulfid, aluminum carbonate or sulfid is not formed ; the products are aluminum hydroxid and carbon dioxid or hydrogen sulfid. The reason for this is that the salts of aluminum with weak acids cannot exist in the presence of water. The hydrolytic action of the water is such as to dissociate the aluminum carbonate or sulfid into aluminum hydroxid and carbonic acid or hydrogen sulfid. These two substances, being volatile, escape from the solution. The equilibrium is thus destroyed so that more of the carbonate or sulfid is dissociated ; the outcome is the complete decomposition into aluminum hydroxid and carbon dioxid or hydrogen sulfid.

377. Aluminum Silicates. Aluminum silicates form a large part of the earth's crust, and in combination with other silicates occur as important minerals. Feldspar is the most abundant, and together with quartz and mica forms granite rock. Under the

action of the weather, the feldspar slowly disintegrates; the chief products are potassium and aluminum silicates. The former, being soluble, is washed away, while the latter is carried by the action of water to places where the current of water slackens its speed, to be deposited as beds of clay. Clay then is aluminum silicate, and is usually mixed with various substances, such as calcium and magnesium carbonates, sand, and the oxids of iron. The better kinds are employed in making stoneware and fire brick; the colored varieties are used in making earthenware and ordinary brick.

Kaolin is the purest form of clay, and is hydrated aluminum orthosilicate. It has a very high melting point when pure, but if mixed with feldspar its point of fusion is lowered sufficiently to make it of use in the manufacture of porcelain.

378. Porcelain. Kaolin is mixed with limestone and sand in such proportions as to prevent the shrinkage of the clay when heated; the ingredients are ground fine and thoroughly mixed. Enough water is added to make the mixture plastic. The mass is then given the desired shapes, carefully dried, and baked at a high temperature in a furnace. A glaze is put on the product by dipping the articles in a mixture of powdered feldspar and quartz suspended in water and again heating or "firing" them. The adhering powder is thus made to melt and form a smooth, impervious, and lustrous coating.

379. Stoneware, Earthenware, and Bricks. Stoneware is a coarse porcelain, and crockery is the best grade of stoneware. The materials for stoneware are not so carefully selected as is the

case with porcelain, and are not heated to so high a temperature. Earthenware is made from ordinary clay. The glaze is put on in various ways. Thus, it may be applied to the earthenware before "firing," or the ware may be heated without a glaze and, towards the end of the operation, salt introduced into the furnace. This volatilizes, comes in contact with the ware, and reacts with it to produce a silicate of sodium and aluminum which melts and forms a glaze.

Bricks consist of unglazed earthenware, although for ornamental purposes a glaze may be put on one or two sides. Their color is mainly due to the presence of iron compounds in the clay.

Exercises and Problems

1. What is the formula of ferric ammonium alum?

2. Terreil, in 1879, found that 0.0455 g. of hydrogen were evolved when 0.410 g. of aluminum were dissolved in an acid. What is the atomic weight of aluminum as calculated from this experiment?

3. Mallet, in 1880, burned the hydrogen evolved by dissolving 10.3691 g. of aluminum in caustic soda, by passing the gas over heated copper oxid, and obtained 10.3515 g. of water. Calculate the atomic weight of aluminum.

TIN AND LEAD

TIN

380. Occurrence. Tin does not occur native, and is almost invariably found in combination with oxygen, forming *tin-stone* or *cassiterite*, SnO_2. This mineral is not widely distributed; most of it comes from a group of islands lying east of Sumatra (Banca, Billiton, and Sinkop).

HISTORICAL NOTE. It is known that the tin mines of Cornwall were worked long before the Christian era, and the metal, both pure and in its alloy (bronze), was extensively used by the ancients.

381. Metallurgy. The tin-stone is crushed, washed free from earthy impurities, and roasted in a reverberatory furnace to drive off sulfur and arsenic. It is again washed and then mixed with powdered anthracite and smelted:

$$SnO_2 + 2C \rightarrow Sn + 2CO$$
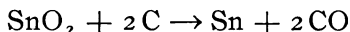
The metal is purified by *liquation*, *i. e.*, it is gradually heated in a furnace with an inclined floor, so that the tin, which melts first, may flow off from the other metals which may be mixed with it and which melt at a higher temperature.

382. Properties. *Physical.* (Table I., Appendix *D*.) Tin is a lustrous, white metal, remaining bright even in moist air. At ordinary temperatures it may be readily beaten out into thin sheets, *tinfoil*,

and may be drawn out into wire. At temperatures near its melting point, however, it becomes brittle enough to be easily powdered.

Chemical. When strongly heated in the air, tin burns with a brilliant light to stannic oxid, SnO_2. Concentrated hydrochloric acid dissolves it slowly, forming hydrogen and stannous chlorid, $SnCl_2$. It reduces hot concentrated sulfuric acid with formation of stannous sulfate and sulfur dioxid:

$$Sn + 2 H_2SO_4 \rightarrow SnSO_4 + SO_2 + 2 H_2O$$
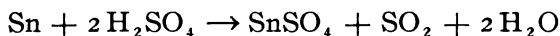
Nitric acid converts it into the insoluble metastannic acid.

383. Uses and Alloys. Tin is extensively used in "tinning" other metals, especially iron, by dipping them into a bath of the molten metal. Tinware utensils consist of sheet iron covered with a thin coating of tin. The copper of cooking dishes is often tinned, and tin-coated brass wire is made into pins. Many useful alloys contain tin. Pewter is three parts tin to one part lead, while solder contains equal parts of both metals. Bronze is a mixture of tin and copper. Tin amalgam is employed in putting the reflecting surface on mirrors.

PRINCIPAL COMPOUNDS OF TIN

Tin forms two series of salts, *stannous*, in which the metal is bivalent; and *stannic*, in which it is quadrivalent.

384. Oxids of Tin. *Stannous oxid*, SnO, a dark brown powder, is unimportant. *Stannic oxid*, SnO_2, is the principal ore of tin, and may be prepared as a white powder by burning tin in the air or by treating the metal with strong nitric acid, evaporating to

dryness and heating the product. When fused with caustic soda, a soluble salt, *sodium stannate*, Na_2SnO_3, is produced, which is used as a mordant in the dyeing of calico.

385. Chlorids of Tin. *Stannous chlorid*, $SnCl_2$, is prepared by dissolving tin in hydrochloric acid. By evaporation of the solution, a white, crystalline compound, $SnCl_2 + 2 H_2O$, separates out, which is called *tin salt*, and is used as a mordant in dyeing. *Stannic chlorid*, $SnCl_4$, is a colorless, fuming liquid, prepared by the action of chlorin on tin or stannous chlorid.

386. Tin Sulfids. Tin foil takes fire in the vapor of sulfur, giving a lead-colored mass of *stannous sulfid*, SnS. When hydrogen sulfid is passed into a solution of stannous chlorid, the same compound is precipitated as a brown powder. *Stannic sulfid*, Sn_2S_3, is prepared by heating tin amalgam, sulfur, and ammonium chlorid together, when it is obtained as a mass of golden yellow scales. It is used as a pigment under the name of *mosaic gold*, and is an ingredient of *bronze powder*. Stannic sulfid is also obtained as a yellow, amorphous precipitate when hydrogen sulfid is passed into an acidified solution of a stannic salt.

LEAD

387. Occurrence. Lead is found native only in small quantities, but is found in many parts of the world combined with sulfur to form *galenite*, PbS. Other minerals are the carbonate, $PbCO_3$ (*cerussite*), and the sulfate, $PbSO_4$ (*anglesite*).

HISTORICAL NOTE. Lead is one of the seven metals known to the ancients. It was often called Saturn, from being associated with the planet of that name.

388. Metallurgy. I. *Precipitation Process.* The galenite is heated with iron, which removes the sulfur:

$$PbS + Fe \rightarrow FeS + Pb$$
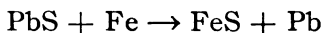
II. *Reduction Process.* Galenite is heated in a reverberatory furnace with free access of air. The sulfid is thus partially oxidized:

$$4\,PbS + 7\,O_2 \rightarrow 2\,PbO + 2\,PbSO_4 + 2\,SO_2$$

The supply of air is then shut off and the temperature raised, when the unchanged lead sulfid reacts with the oxid and sulfate:

$$2\,PbO + PbS \rightarrow 3\,Pb + SO_2$$
$$PbSO_4 + PbS \rightarrow 2\,Pb + 2\,SO_2$$
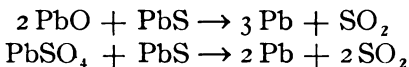
389. Properties. *Physical.* (Table I., Appendix *D.*) Lead is a soft, bluish-white metal which cannot be hammered out into foil or drawn into wire, but is obtained in these forms by rolling and pressing. A freshly-cut surface is highly lustrous, but on exposure to the air soon becomes tarnished. When a solution of a lead salt is electrolyzed or has a piece of zinc suspended in it, the metal separates in the form of beautiful, lustrous crystals.

Chemical. Lead dissolves readily in dilute nitric acid, but sulfuric and hydrochloric acids are almost without action upon it. It is unaffected by pure water in the absence of air, but in contact with air lead hydroxid is formed, which is slightly soluble in water. If the water is hot or contains carbon dioxid or ammoniacal salts, lead is dissolved much more abundantly. As lead salts are poisonous, drinking water which contains even traces of such substances, and which is conveyed in lead pipes,

should not be used until it has run for some time so as to cover the metal with a coating of the insoluble hydroxid and carbonate.

390. Uses and Alloys. Because of the ease with which lead can be worked and its power of resisting acids, it is used in lining sulfuric acid chambers and some of the cells used in electrolytic processes. As in contact with water it soon becomes coated with an impervious and insoluble layer of hydroxid and carbonate, it is also extensively used in making water pipes. These are made by squeezing hot lead under great pressure through ring-shaped apertures of steel. Ordinary shot is an alloy of lead with a little arsenic. Type metal and solder are also lead alloys.

SOME IMPORTANT COMPOUNDS OF LEAD

Lead, like tin, forms two series of salts; the bivalent series is distinguished as *plumbous* (this word is but seldom used), and the quadrivalent series is known as *plumbic*.

391. Oxids of Lead. Five oxids of lead are known: Lead suboxid or plumbous oxid, Pb_2O, plumbic oxid (lead monoxid, massicot, litharge), BbO, lead sesquioxid, Pb_2O_3, triplumbic tetroxid (red lead, minium), Pb_3O_4, and plumbic peroxid (lead dioxid), PbO_2.

Plumbic oxid is obtained when lead is heated with free access of air, or when lead nitrate or carbonate or any of the other oxids are strongly heated. It forms a yellow powder commercially known as *massicot*, which when melted and again solidified yields a crystalline mass known as *litharge*. It is

used in the manufacture of some varnishes and oils, other lead compounds, flint glass, and as a glaze for earthenware.

Red lead is formed when lead carbonate or monoxid is heated to above 400°. It is a red powder used as a common red paint and in making certain cements and varnishes as well as flint glass.

Lead dioxid is prepared by the action of dilute nitric acid on red lead. It is a brown powder, giving up its oxygen readily, so that it is a powerful oxidizing agent. It is used in storage batteries.

392. Chlorids of Lead. *Lead chlorid*, $PbCl_2$, is obtained as a white precipitate when a soluble metallic chlorid is added to a solution of a lead salt; also by the action of boiling hydrochloric acid on lead. It is somewhat soluble in cold water, and freely so in hot water. *Lead tetrachlorid* is obtained as a yellow, unstable liquid when lead dioxid is dissolved in strong, cold hydrochloric acid.

393. Lead Sulfate, $PbSO_4$. Lead sulfate is formed when a soluble sulfate is added to a solution of some lead salt. It is a white, insoluble powder, sometimes used as an adulterant of white-lead paint.

394. Lead Nitrate, $Pb(NO_3)_2$. Lead nitrate is obtained by dissolving lead or litharge in dilute nitric acid. It forms white crystals freely soluble in water. When heated it decomposes into litharge, nitrogen peroxid, and oxygen.

395. Lead Sulfid, PbS. Lead sulfid occurs naturally as galenite and may be obtained as a black precipitate by passing hydrogen sulfid into a solution of a lead salt. When heated in the air it is oxidized to lead sulfate.

396. Lead Carbonates. (*White Lead.*) When ammonium carbonate solution is added to a solution of lead nitrate or acetate, a white, crystalline powder is precipitated, which is lead carbonate, $PbCO_3$. Sodium or potassium carbonate precipitates from lead solutions *basic* carbonates, varying somewhat in composition. The most important of these is *white lead.* This compound is a valuable ingredient of paint and is manufactured by several processes; the best and longest known is the Dutch method.

Dutch Method. The lead is cast into gratings called " buckles," which are placed in earthenware pots. A little vinegar or dilute acetic acid is added and the pots are placed on a thick layer of spent tanbark upon the floor of a shed. The pots are covered over with planks, upon which is placed more tanbark and a second tier of pots. This is continued up to the roof of the shed. The tanbark ferments and thereby becomes heated so that the acid is gradually vaporized and attacks the lead, and the carbon dioxid which is liberated also attacks the metal. The reactions are complicated and not well understood. In three or four months the process is complete. The contents of the jars are then sifted so as to separate the white lead from the unattacked lead and the product ground with water and dried. The value of white lead is due to its " body " or covering power. It is very poisonous and turns black in air containing hydrogen sulfid.

Other Methods. In the *German process* sheets of lead are hung up and a mixture of steam, carbon dioxid, and the vapor of acetic acid blown over them. In the *French process* carbon dioxid is passed into a solution containing lead acetate and oxid.

397. Lead Acetate, $Pb(C_2H_3O_2)_2$. Lead acetate is formed by dissolving lead in dilute acetic acid. It is a white, crystalline salt with a sweetish taste, and is commonly called "sugar of lead."

Exercises

1. Why is white-lead paint not suitable for covering the walls of a chemical laboratory?

2. What three insoluble chlorids have thus far been studied? In what liquids are they soluble?

3. What valency has each of the metals in each of the following compounds: $ZnBr_2$; SbH_3; $AuCl_3$; CdO; $SnCl_4$; Al_2O_3; $BaCO_3$; $LiCO_3$; KNO_3?

Problems

1. (a) Van der Plaats, in 1885, found that 45.8323 g. of tin, when oxidized, gave 58.2519 g. of SnO_2. If the atomic weight of oxygen is 16.00, what is that of tin?

(b) The same investigator also found that on reducing 17.2935 g. of SnO_2 with hydrogen, 13.6056 g. of metal were obtained. What is the atomic weight of tin?

2. Dumas found that the chlorin in 4.504 g. of tin chlorid was equivalent to 7.481 g. of silver. If the atomic weights of silver and chlorin are 107.94 and 35.45, respectively, what is the atomic weight of tin?

3. Dumas, in 1859, obtained from 28.409 g. of tin 36.121 g. of its oxid. What is the atomic weight of tin?

4. Dumas, in 1859, added to a solution containing 4.504 g. of stannous chlorid an excess of a solution of silver nitrate and found that the precipitate of silver chlorid formed contained 7.481 g. of silver. What is the atomic weight of tin, it being assumed that the atomic weights of chlorin and of silver are 35.43 and 107.94, respectively?

5. How many pounds of lead and of sulfur are contained in 800 pounds of galenite, PbS?

CHAPTER XXVIII

COPPER, SILVER, GOLD, AND PLATINUM

COPPER

398. Occurrence. Copper occurs native in several places, notably in the Lake Superior region. Its principal minerals are *chalcocite*, Cu_2S, *chalcopyrite*, $CuFeS_2$, *malachite*, $CuCO_3$, $Cu(OH)_2$, and *ruby copper* or *cuprite*, Cu_2O.

HISTORICAL NOTE. Copper has been known from the earliest times. Alloyed with tin, it forms bronze, which was used to make weapons, before the art of extracting iron from its ores was invented.

399. Metallurgy. I. *Dry Way.* The sulfid ores are partially converted into oxids by roasting, and then strongly heated, when the following reaction ensues:

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$
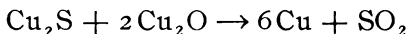
II. *Wet Way.* The ores are converted into the soluble chlorid by heating with common salt, or into the soluble sulfate by treatment with a solution of iron sulfate. The copper is then thrown out of solution by metallic iron or by electrolysis.

PURIFICATION OF COPPER. The crude copper thus obtained is usually purified by electrolysis. The copper is cast into thick plates which are suspended in a solution of acidified copper sulfate. Thin sheets of pure copper are also hung in the solution. The crude copper sheets are made the anodes, and pure copper sheets the cathode of a powerful electric current. Pure copper is deposited from the solution on the cathode and

an equivalent amount of copper dissolved from the anode. The concentration of the solution thus remains unchanged, while the copper passes from anode to cathode. The impurities of the crude copper fall down beneath the anode, forming the so-called "anode-mud," from which gold and silver are obtained in paying quantities. This "electrolytic copper" is very pure.

400. Properties. *Physical.* (Table I., Appendix *D.*) Copper is a reddish metal with considerable ductility and tenacity, and is an excellent conductor of heat and electricity.

Chemical. Copper is unaffected by dry air except when heated to nearly a red heat, when it combines with oxygen to form the black oxid of copper, CuO. In moist air it slowly becomes covered with a green coating, *verdigris*, which is a hydrated copper carbonate. It burns in chlorin, but is only slowly acted upon by hydrochloric acid. Nitric acid dissolves it with formation of nitrogen oxids and copper nitrate, $Cu(NO_3)_2$; sulfuric acid does the same, producing the sulfate, $CuSO_4$, and sulfur dioxid. Vegetable acids, fats, and common salt act upon copper when exposed to the air, and since copper salts are poisonous, eatables containing vinegar or salt should not be preserved in copper utensils.

401. Uses and Alloys. Copper is used extensively in many ways, such as in conductors for electric currents, in making coins and stills, in covering roofs and ships' bottoms. Some kinds of engravings, maps, and etchings are prepared on copper plates, and books are printed and illustrated from an electrotype prepared by depositing a thin coating of copper in a mold of the type or design. Copper also enters into the composition of a number of

valuable alloys. *Brass* is a mixture of copper and zinc in proportions varying according to the kind of brass desired. *Gun metal* and *bell metal* are alloys of tin and copper. *German silver* is an alloy of copper, zinc, and nickel.

SOME IMPORTANT COMPOUNDS OF COPPER

Copper forms two series of compounds, in one of which (cuprous) it is univalent, and in the other (cupric), bivalent.

402. Copper Oxids. *Cuprous oxid*, Cu_2O, is a red substance insoluble in water.

Cupric oxid, CuO, is made by heating copper to redness with free access of air, and by heating copper nitrate or carbonate or hydroxid; the last-named compound is formed when a fixed alkali solution is added to a solution of a copper salt:

$$CuSO_4 + 2\,KOH \rightarrow Cu(OH)_2 + K_2SO_4$$
$$Cu(OH)_2 \rightarrow CuO + H_2O$$
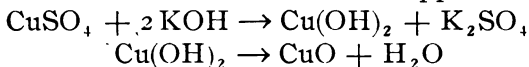
403. Copper Sulfate, $CuSO_4 + 5\,H_2O$. Copper sulfate is made by the action of hot concentrated sulfuric acid on copper, and is also obtained as a by-product in the refining of gold and silver. It is commercially known as "blue vitriol," and is used extensively in copper-plating, in galvanic batteries, and in making paint. Its five molecules of water of crystallization can be expelled by heating, leaving a grayish residue of anhydrous copper sulfate, which turns blue when brought in contact with water.

404. Copper Nitrate, $Cu(NO_3)_2$. When nitric acid acts on copper, the acid is reduced and a very soluble, blue salt is produced. When heated, it decomposes into cupric oxid and oxids of nitrogen.

405. Copper Sulfid, CuS. Copper sulfid is formed as a black precipitate when hydrogen sulfid or an alkalin sulfid is added to a solution of a copper salt.

COPPER-PLATING. Copper-plating consists in depositing upon an object a coating of copper. An iron wire placed in a copper sulfate solution in a short time becomes covered with a coating of copper. Usually, however, the plating is effected by means of electrolysis, and the process is extensively used in electrotyping, or the reproduction of type and cuts. A plaster of Paris or wax mold is made of the type, and dusted over with finely powdered graphite so as to make it conduct electricity. This is placed in a solution of copper and made the cathode of an electric current, of which the anode is a copper plate. When the current passes, copper is deposited on the mold and a perfect reproduction of the type is obtained as a thin coat of copper. This is removed from the mold and type metal poured into it so as to give the electrotype the required strength and firmness.

SILVER

406. Occurrence. Silver occurs native, sometimes in large masses, but usually in crystalline threads and scales in the fissures of rocks. Besides in *horn silver*, AgCl, it occurs in combination with sulfur, as *argentite*, Ag_2S, and *pyrargyrite*, Ag_3SbS_3. The principal silver mines are in Mexico, South America, Colorado, Nevada, Australia, and India, although a good deal of silver is obtained from lead ores, with which it is mixed in small proportions.

HISTORICAL NOTE. Silver was one of the seven metals of the ancients. It was called *luna* by the old chemists because its color was fancied to resemble that of the moon (the Latin word for moon is *luna*). This name is perpetuated in the common name for silver nitrate, *lunar* caustic.

407. Metallurgy. I. *Amalgamation Process.* The ore is crushed, mixed with common salt and roasted. The silver chlorid thus formed is shaken up in revolving cylinders with scrap iron, mercury, and water. The iron takes the chlorin from the silver, which then forms an amalgam with the mercury. The mercury is separated from the silver by distillation.

II. *Zinc or Parkes' Process.* Silver is also separated from lead by means of zinc, which is but very slightly soluble in lead. The lead containing silver is melted in large tanks and slabs of zinc thrown in. These float about and gather together all of the silver. The alloy thus formed is removed and distilled; the zinc passes off and leaves the silver.

CUPELLATION. When lead contains a considerable proportion of silver, this may be extracted by heating the alloy in a *cupel*, a shallow dish made of bone ash. The lead oxidizes and the lead oxid melts and is absorbed by the porous bone-ash cupel, leaving the silver. This process is especially used in the analysis technically called *assay* of silver ores.

408. Properties. *Physical.* (Table I., Appendix *D*.) Silver is the whitest of the metals and has a very high luster; its polished surface is one of the best reflectors of light. It is very malleable and ductile, and is the best known conductor of heat and electricity.

Chemical. Silver does not oxidize in the air at any temperature under ordinary pressures, though molten silver dissolves oxygen, which is given off when it solidifies. The tarnishing of silverware is due to the action of hydrogen sulfid which is often present in minute proportions in the atmosphere.

"Oxidized" silver is really "sulfidized" silver; it is formed by the action of a soluble sulfid on silver. Dilute nitric acid and hot sulfuric acid convert silver into the nitrate, $AgNO_3$, and sulfate, Ag_2SO_4, respectively; the acids themselves are reduced and do not give up hydrogen. Silver is not dissolved by hydrochloric acid, as its chlorid is insoluble.

409. Uses and Alloys. The main applications of silver are in coinage, jewelry, and tableware. Pure silver is too soft for these purposes and hence it is alloyed with copper, which makes it harder and more durable. Each country fixes by law the ratio of silver to copper in its coinage; usually it is 90 to 10. "Sterling silver" also contains about these proportions.

SILVER-PLATING. Silver-plating was at first done by covering some metal or alloy with a thin plate of silver, which was made to adhere by passing the sheets between rollers. The plating was also done by covering the object with silver amalgam and then driving off the mercury by heat, as well as by rubbing the article with a mixture of silver chlorid, common salt, chalk, and potash. Nowadays it is almost universally done by electrolysis. The article is attached to the cathode of an electric circuit and suspended in a solution of silver cyanid, $AgCN$, containing potassium cyanid, KCN, while a plate of silver forms the anode. "Frosted silver" is obtained by dipping the hot metal into sulfuric acid for a few moments.

Mirrors are silvered by placing them in a bath containing some silver compound and a reducing agent.

SOME IMPORTANT COMPOUNDS OF SILVER

410. Properties. Silver is always univalent. Its compounds are usually white, and many of them undergo decomposition when exposed to

light. The Latin name of silver, *argentum*, is often used in naming its compounds, as *argentic* nitrate.

SILVER OXID, Ag_2O. Silver oxid may be prepared by mixing strong solutions of silver nitrate and potassium hydroxid. The hydroxid at first precipitated soon loses water and becomes changed into the oxid. Silver oxid is a dark brown, heavy powder, slightly soluble in water; the solution is feebly alkalin. When heated it breaks up into silver and oxygen (§ 30). A solution of the oxid in ammonium hydroxid deposits crystals of an explosive compound known as "fulminating silver."

411. Silver Nitrate, $AgNO_3$. Silver nitrate is made by dissolving silver in hot and dilute nitric acid. By evaporating the solution, colorless crystals are obtained. These, when melted and cast into sticks, form " lunar caustic," used by surgeons to cauterize flesh. Silver nitrate in solution is decomposed by organic compounds, yielding silver as a fine black powder. Indelible ink is a solution of silver nitrate in water containing a little gum. Hair dyes also frequently contain this salt.

412. Silver Chlorid, AgCl. Silver chlorid occurs in nature as the mineral, horn silver, so called because of its tough, horn-like texture, and is obtained as a white precipitate when any solution of a soluble chlorid is added to a solution of a silver salt. It is soluble in ammonium hydroxid and in solutions of the alkalin thiosulfates.

413. Silver Bromid, AgBr, **and Iodid,** AgI. Silver bromid and iodid may be prepared by adding any soluble bromid or iodid to a silver nitrate solution. They are both yellow, insoluble compounds. They differ from silver chlorid in not being very soluble in ammonium hydroxid.

PHOTOGRAPHY

ACTION OF LIGHT. Photography is based on the fact that light brings about the decomposition of the halid salts of silver. Although this fact was known as early as the sixteenth century, yet the art was not developed until nearly the middle of the nineteenth century, when Daguerre discovered the action of the developer. The art of photography as now practiced is essentially as follows. It involves : First, the preparation of the *negative*, and second, the printing of the *positive*.

THE NEGATIVE. Glass plates are covered with a mixture or emulsion of gelatin and silver bromid or iodid ; the operation is carried out in a room but dimly lighted with red light, which has a very slow action on silver salts. These gelatin-bromid plates are packed in light-tight boxes, and are introduced into the camera, of which there are a multitude of forms on the market, with the film side next the lens. During the exposure no picture appears on the plate. This is first brought out by the *developer*. To develop the picture it is placed in a solution of a developer, such as pyrogallic acid with sodium carbonate. Those parts affected by the light are now made visible and the picture appears, but with the lights and shadows reversed. The next operation is that of *fixing* and consists in dissolving out the halid salt which has not been affected by the light. A solution of sodium thiosulfate ("hyposulfite") is used for this purpose. The negative is now complete and shows the picture with its light parts dark and its dark parts light.

THE POSITIVE. Paper is covered on one side by a layer or film of albumen which is *sensitized* by depositing in it silver chlorid. This is done by first floating the paper on sodium chlorid solution and then on silver nitrate solution ; silver chlorid is thus produced right in the albumen by the reaction of the two salts. The sensitized paper is placed with its film against that of the negative in a "printing frame" and exposed to sunlight. The picture thus *printed* is next *toned* and *fixed*. Toning consists in dipping the positive in a solution of

gold or platinum chlorid whereby the silver is partially replaced by the gold. Fixing is done with sodium thiosulfate, as in the case of the negative.

GOLD

HISTORICAL NOTE. Gold has been known since the earliest times. Owing to the yellow color of both, it was supposed by the ancient chemists that there was some connection between it and the sun. For many centuries it was the aim of chemists, or rather alchemists, to convert substances into gold, the noblest of the metals. They fancied that there might be prepared a substance which they called the Philosopher's Stone, that would effect this transmutation.

414. Occurrence. In small quantities gold is found native in many localities, principally, however, in California and some other western states, Australia, Siberia, South Africa, and Alaska. It is rarely found in combination. The native gold occurs mainly in the veins of quartz rocks. As these are disintegrated by the weather, the quartz sand and gold are carried down creeks and rivers and deposited where the current runs slowest.

415. Metallurgy. Several methods are in use. *Placer mining* consists in washing earth, gravel, and sand that contain gold in a rapid current of water, which carries away the lighter particles.

In *hydraulic mining* a powerful stream of water is thrown against a gravel bank, and the water carries away the disintegrated material down through long wooden troughs or "sluices" in which are placed cross-pieces of wood. These catch the heavier particles, while the lighter ones are swept along. The heavy particles obtained in both placer and hydraulic mining are treated with mercury, with

which the gold forms an amalgam, and this is sep-
arated and distilled, leaving the gold in the retort.

In *quartz mining* the gold-bearing rock is crushed
to a powder in "stamp mills," and the gold separated
as in hydraulic mining.

In the *cyanid process* the ore is pulverized and
treated with potassium cyanid solution which dis-
solves the gold. It is thrown out of solution by
the addition of iron.

SEPARATION OF GOLD FROM SILVER. Usually gold
ores contain silver as well, and the product obtained is
an alloy of these metals. If gold does not form more
than a *quarter* of the alloy, the silver can be dissolved
out by boiling with sulfuric acid. This process is
accordingly known as *quartation*. When but little
silver is present, the alloy is dissolved in *aqua regia*
and the gold thrown out of the diluted solution by the
addition of iron sulfate.

The *Electrolytic Method* is coming into use. The
anode consists of an alloy of gold and silver. The
cathode is silver, and the electrolyte is nitric acid.
When the circuit is closed, the silver of the anode goes
into solution, leaving the gold as a fine powder, which is
caught in a cloth bag which surrounds the whole anode.

416. Properties. *Physical.* (Table I., Appen-
dix *D*.) Gold is a yellow metal with very brilliant
luster; it is the most malleable and ductile of all the
metals, and is a very good conductor of heat and
electricity.

Chemical. Gold is not acted upon by any ele-
ments excepting the halogens, and is soluble only
in aqua regia.

417. Uses and Alloys. Gold is extensively used
in jewelry and money. The pure metal is too soft
to withstand much usage; hence it is alloyed with

silver or copper or both, according to the shade of color and the degree of hardness desired. United States coins contain 900 parts gold to 100 of copper and are said to be "900 fine." Jewelers express the relative purity of gold in *carats*. Thus, 24-carat gold is pure, 18-carat gold contains $\frac{18}{24}$ gold, 14-carat, $\frac{14}{24}$ gold, and so on. Considerable gold in the form of "gold leaf" is used as fillings for teeth and for gilding ornamental work on book covers, signs, furniture, and buildings.

GOLD-PLATING. Gold-plating is usually done by electrolysis; a solution of gold in potassium cyanid is used as the electrolyte.

418. Compounds of Gold. Gold dissolves in aqua regia with formation of auric chlorid, $AuCl_3$, used in "toning" in photography. Auric chlorid, when heated, loses chlorin and is converted into aurous chlorid, $AuCl$. If stannous chlorid, $SnCl_2$, solution be mixed with a solution of auric chlorid, a purple-colored precipitate, known as *purple of Cassius*, is formed.

PLATINUM

419. Properties. Platinum is found in the Ural Mountains either free or alloyed with some of the rare metals, iridium, palladium, rhodium, ruthenium, and osmium. It is a white, lustrous metal, very malleable and ductile, and melts only at the highest temperatures. Acids have no action upon it, but aqua regia dissolves it, forming platinum chlorid, $PtCl_4$, which is used in "toning" in photography. Platinum is attacked by alkalin hydroxids. It is used in making stills, crucibles, foil, and wire for the laboratory.

NOTE. When platinum chlorid is heated to redness the chlorin is driven off, leaving the platinum in a very finely divided state. This *spongy platinum*, as well as a finer form called *platinum black*, has the property of adsorbing or occluding gases. Oxygen thus occluded is much more energetic than ordinary oxygen.

Exercises

1. How has cupric oxid been employed in verifying the Law of Definite Proportions by mass or weight?

2. If given an ore supposed to contain silver, how would you make a test for the presence of that metal?

3. Write the equation for the reaction between hot concentrated sulfuric acid and copper.

4. Why is it customary to employ a wooden and not a silver mustard spoon?

Problems

1. How many grams of silver nitrate would be required to make 20 g. of silver chlorid?

2. Hampe, in 1874, reduced 20.6885 g. of copper oxid in hydrogen and obtained 16.5167 g. of copper. Calculate the atomic weight of copper.

3. How many grams of silver nitrate can be prepared by dissolving 15 g. of silver in nitric acid, evaporating to dryness, and melting the residue?

4. What is the value of the silver in 10 kg. of a 10 per cent solution of silver nitrate, if one ounce of silver is worth 60 cents?

5. Stas burned 101.519 g. of silver in a current of chlorin and obtained 134.861 g. of silver chlorid. What are the combining weights of silver and chlorin?

6. Richards, in 1889, dissolved 4.39313 g. of copper in silver nitrate solution, whereby 14.9104 g. of silver were precipitated. If the atomic weight of silver is 107.94, calculate that of copper.

7. Shaw, in 1887, passed the same electric current through solutions of copper and silver salts and found the ratio of the weights of the metals precipitated to be 1 : 3.4000, respectively. Taking the atomic weight of silver as 107.94, calculate that of copper.

8. From 10 $c.c.$ of a solution of silver nitrate 0.9365 g. of silver chlorid were obtained by precipitation with hydrochloric acid. How many grams of silver nitrate are contained in a liter of the solution?

IRON, NICKEL, AND COBALT

IRON

420. Occurrence. Iron is not only the most useful of the metals, but is also one of the most abundant and most widely distributed. Native iron occurs but rarely; meteorites contain a large proportion of the pure metal.

The principal ores of iron are *magnetite* (*lodestone*), Fe_3O_4; *hematite*, Fe_2O_3; *limonite*, a hydrated oxid, and *siderite* (*spathic iron ore*), $FeCO_3$. *Iron pyrites* (*fool's gold*), FeS_2, although very abundant, cannot be used in obtaining the metal because of the objectionable properties communicated to iron from even a very slight admixture of sulfur. It is used extensively as a source of sulfur in the manufacture of sulfuric acid (§ 278).

421. Metallurgy. The ores of iron are oxids, hydroxids, or carbonates, and are reduced by heating them with carbon in the form of charcoal, coke, or coal. The chief impurity of the ores is sand (silica). As this can combine with iron to form iron silicate, to prevent the loss of the metal thus occasioned, limestone (calcium carbonate) is added to the mixture of carbon and ore, whereby the silica combines with the calcium instead of the iron. The molten calcium silicate, or slag, does not mix with melted iron, but floats upon it.

Fig. 37 — A MODERN BLAST FURNACE IN OPERATION

The reduction is effected in a blast furnace (Fig. 37). This is a structure about seventy feet high, made of plates of iron bound together and lined with fire brick. The furnace is nearly filled from the top with the ore, fuel, and limestone; a

little of each is added at a time so as to secure a thorough mixing of the three substances. A powerful blast of heated air is blown in through pipes called *tuyeres* (pronounced *twcers*) near the bottom. As the reduction of the metal proceeds, it collects as a liquid at the bottom of the furnace with the molten slag floating upon it. Every few hours the slag and the iron are drawn off; the latter is run out into molds where it solidifies into bars called "pigs"; the metal itself is known as "pig iron." Charges of fuel, ore, and limestone are introduced into the top of the furnace at frequent intervals; its operation is thus made continuous for months and even years.

422. Chemistry of the Process. The chemical reactions involved in the reduction are the following: The carbon of the fuel in the lower part of the furnace unites with the oxygen of the air forced in to form carbon dioxid, which, as it passes through the highly heated fuel above it, is reduced to the monoxid. The carbon monoxid unites with the oxygen in the ore, forming carbon dioxid, while the iron is set free:

$$Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2$$
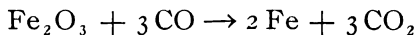
The gases which pass from the reacting mixture still contain about 25 per cent of carbon monoxid. These are drawn off just below the top of the furnace and are conducted to the boiler house, where they are burned to generate steam for the engines producing the blast of air.

423. Varieties of Iron. The iron we use and speak of is not pure, but contains small proportions of other elements which greatly vary its properties.

Carbon has the greatest influence upon the properties of iron, and silicon has a similar but less intense effect. Sulfur, even in very small relative amounts, makes iron brittle when hot, and hence useless for forging. Phosphorus renders iron brittle at ordinary temperatures. Certain metals, notably manganese, chromium, and nickel, give steel some very desirable properties.

424. Cast Iron. Cast iron contains from 2 to 7 per cent of carbon, and usually 2 to 3 per cent of other elements. If most of the carbon is chemically combined with the iron, the metal is known as *white cast iron*. But sometimes, especially when the molten metal has cooled slowly, some of the carbon forms graphite which imparts a darker color to the iron, which is hence called *gray cast iron*. The latter variety is softer than the former and melts at a lower temperature. Cast iron is too brittle to be welded, and melts at a much lower temperature than pure iron. It is extensively used in making castings. For that purpose it is melted in a small blast furnace, and the molten metal poured into sand molds. The presence of manganese makes it coarsely crystalline, and it is then known as *spiegeleisen* or *ferro-manganese*.

425. Wrought Iron. Wrought iron is prepared from cast iron by heating it in puddling furnaces. This furnace is of the reverberatory type (Fig. 28), and has a layer of ferric oxid, Fe_2O_3, placed underneath the cast iron. As the flames play over the mixture the cast iron melts and its carbon combines with the oxygen in the oxid. The mixture is continually stirred about or "puddled," and as the

carbon burns out, the purified iron, melting as it does at a higher temperature than cast iron, becomes of a pasty consistency. The puddler shapes the pasty iron into large balls which are removed from the furnace and squeezed in rollers or hammered into sheets. Wrought iron is also made by the open-hearth process (§ 429).

Wrought iron contains less than one-half per cent of carbon. It is tough and malleable and can be forged or welded, but not cast or tempered. It is often called *malleable* iron, and is made into wire nails, bolts, chains, tires, horseshoes, and so on.

426. Steel. Steel contains more carbon than wrought iron, but less than cast iron. It is malleable and fusible, and can be forged, welded, and cast. It is harder than wrought iron and stronger than cast iron. By appropriate treatment it can be *tempered, i. e.*, made to acquire varying degrees of hardness. If steel be heated to a red heat and then suddenly cooled by immersing it in water or oil, it becomes less malleable but much harder, and can take and hold a sharp edge. If such tempered steel be heated again and then slowly cooled, it becomes relatively soft; it is annealed; the temper is "drawn." Any degree of hardness may be obtained between these extremes. Instruments require different tempers according to their application. Thus, ordinary cutlery is tempered and then heated to about 250°, when a brown film of oxid appears; part of the temper is thereby drawn and the steel, while hard enough for cutting purposes, becomes less brittle. Watch-springs after tempering are heated to nearly 300°, when a blue film appears.

427. Manufacture of Steel. As it is the carbon contained in steel which mainly determines its properties, the aim in its manufacture is to give iron the desired proportion of carbon, and at the same time to eliminate such substances as sulfur, phosphorus, and silicon, which impart undesirable properties, or to add other elements as manganese or nickel, which give certain desirable qualities to the steel. In the *cementation* or *crucible process* bars of wrought iron are imbedded in finely powdered charcoal and kept at a red heat for a week or more. The carbon penetrates the iron, producing a very fine quality of steel, especially adapted for making tools. The expense of the process, however, is prohibitive for most purposes.

NOTE. Harveyized steel is made by packing steel in a mixture of charcoal and boneblack, and raising to a high temperature. This operation makes the outside of the steel very hard, so that it is adapted for armor plate for war vessels.

428. Bessemer Process. The *Bessemer process* consists essentially in reducing pig iron in a "converter" to wrought iron, and then adding enough iron containing a known amount of carbon to bring the proportion of carbon up to the desired point.

The converter (Fig. 38) is a large pear-shaped furnace mounted on axes or trunnions so that it may be inverted. The converter is made of iron plates bound together and lined with ganister, a very infusible, siliceous earth. The bottom of the converter is perforated with a number of small holes, up through which a blast of air may be forced. A charge of ten to twenty tons of molten cast iron is introduced into the converter, and air
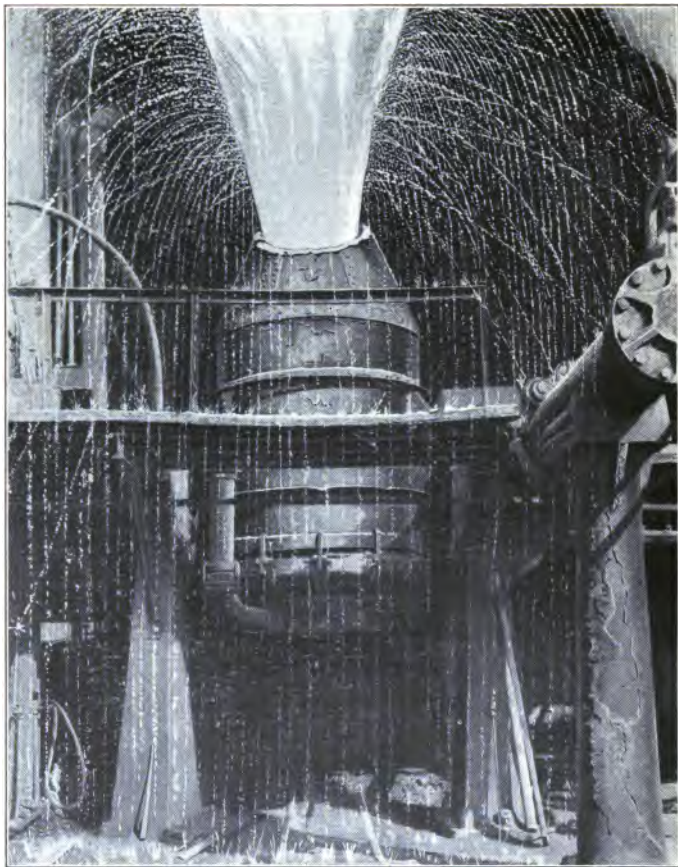
Fig. 38 — A BESSEMER CONVERTER WHILE THE BLAST IS ON

blown up through it. The heat generated by the burning of the impurities in the cast iron is sufficient to keep the metal liquid, and in about half an hour it is converted into wrought iron. A weighed amount of spiegel iron is now thrown

into the converter and in a few moments the converter is turned over and the steel formed run out into molds.

BASIC-LINING PROCESS. Phosphorus is an objectionable constituent of steel; hence it is necessary in the Bessemer process to employ a cast iron practically free from that element. It may be removed, however, by lining the converter with a mixture of lime and magnesia instead of ganister; the latter is acid, while the former is basic. The phosphorus pentoxid produced by the burning unites with the lime and magnesia, forming phosphates which are not reduced by the iron. Cast-iron containing phosphorus may therefore be used, as the phosphorus is thus eliminated from the steel. The slag (Thomas slag) obtained consists of a basic phosphate which, when finely ground, has great value as a fertilizer.

429. Open-Hearth Process. Pig iron is mixed with wrought iron or steel scrap and heated in a reverberatory furnace with an oxidizing gas flame (Figs. 39 and 40). When enough carbon has been burned out, spiegel iron is added, or about every quarter-hour a sample is taken from the furnace and analyzed for carbon; the operation is at an end when the right amount of carbon is present. The steel made by this process is very tough and elastic, so that although the process is more expensive than the Bessemer, it is nevertheless a successful rival.

430. Properties of Iron. *Physical.* (Table I., Appendix *D.*) Pure iron is a silvery white, lustrous metal; it is the most magnetic element, losing its magnetism readily, however, while steel holds it permanently.

Chemical. Chemically pure iron is prepared by reducing the oxid or chlorid in a current of hydrogen.

Fig. 39 — FRONT VIEW OF AN OPEN-HEARTH FURNACE

When this reduction takes place at as low a temperature as possible, the iron is so finely divided that it takes fire when exposed to the air at ordinary temperatures; it is *pyrophoric*. In dry air iron is not affected, but in moist air it rusts, forming ferric hydroxid, and as the rust does not form a compact protective coating to the iron, the latter is in time totally converted into the former.

As water dissociates at high temperatures, its oxygen will combine with red-hot iron to form the magnetic oxid, Fe_3O_4, and its hydrogen will be set free.   As this oxid is reduced by hydrogen, a state of equilibrium results:

$$3\ Fe + 4\ H_2O \rightleftarrows Fe_3O_4 + 4\ H_2$$
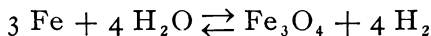
Iron is soluble in dilute hydrochloric and sulfuric acids with evolution of hydrogen and formation of

the chlorid and sulfate, respectively. It reduces rather dilute nitric acid with formation of nitric oxid, but if it be dipped in concentrated nitric acid and then rinsed off, it is not acted upon by the diluted acid; it is converted into the so-called "passive state."

COMPOUNDS OF IRON

431. Some Important Ferrous and Ferric Compounds. Iron forms two classes of compounds. It is bivalent in *ferrous* compounds and trivalent in *ferric*. A ferrous compound when acted upon by an oxidizing agent, such as oxygen, nitric acid, or potassium chlorate, passes into the corresponding ferric compound, and this in turn reverts to the original ferrous compound when acted upon by reducing agents such as hydrogen.

Fig. 40 — REAR VIEW OF AN OPEN-HEARTH FURNACE

432. **Oxids and Hydroxids.** *Ferrous oxid*, FeO, is prepared by reducing ferric oxid at about 300°. It is a black powder which oxidizes very readily. *Ferrous hydroxid*, $Fe(OH)_2$, is precipitated by the addition of an alkalin solution from ferrous salt solutions. It is of a pale green color, but oxidizes rapidly into brown ferric hydroxid.

Ferric oxid, Fe_2O_3, is the mineral hematite. It may be prepared by heating ferric hydroxid or ferrous sulfate, and forms a dark red powder. It is a by-product of the manufacture of fuming sulfuric acid and of galvanized iron and tin ware. Under the names of *rouge* and *Venetian red* it is used to polish glass and jewelry and to make red paint.

Ferric hydroxid is thrown down as a reddish-brown precipitate when ammonium or an alkali metal hydroxid is added to a ferric salt in solution. When red-hot iron is exposed to steam, ferric oxid is formed; it protects the iron within from the action of the weather.

Ferrous-ferric oxid, Fe_3O_4, occurs as the mineral magnetite (lodestone). It is black and strongly magnetic, hence the name "magnetic oxid."

433. **Iron Sulfids.** *Ferrous sulfid*, FeS, is a black solid prepared by adding an alkalin sulfid to a solution of a ferrous salt or by heating a mixture of iron and sulfur.

Iron pyrites, FeS_2, is of the color of brass. Crystals of it are often found in rocks, and from its often being taken for gold it has received the popular name of "fool's gold." Its sulfur oxidizes to sulfur dioxid when it is heated; it is used in the manufacture of sulfuric acid.

434. Iron Chlorids. *Ferrous chlorid*, $FeCl_2$, is formed when iron interacts with hydrochloric acid. It crystallizes from solution in green prisms containing four molecules of water. It may be prepared in the anhydrous state as a white powder when iron is heated in dry hydrogen chlorid.

Ferric chlorid, $FeCl_3$, is formed as a yellowish-brown mass when chlorin is passed over red-hot iron. It is very deliquescent, and may be prepared in solution by passing chlorin into a solution of ferrous chlorid.

435. Iron Sulfates. *Ferrous sulfate*, $FeSO_4$, is formed by interaction of iron or ferrous sulfid with dilute sulfuric acid. It crystallizes with seven molecules of water, forming green crystals known as *green vitriol* or *copperas*. It is used as a disinfectant, in making inks, and in dyeing.

Ferric sulfate, $Fe_2(SO_4)_3$ is obtained in solution by the oxidizing action of nitric acid on a solution of ferrous sulfate.

436. Potassium ·Ferro- and Ferri-Cyanids. *Potassium ferrocyanid*, $K_4Fe(CN)_6 + 3H_2O$ (*yellow prussiate of potash*) forms large yellow crystals soluble in water. Heated with dilute sulfuric acid it gives prussic acid, and with concentrated sulfuric acid, carbon monoxid. When its solution is mixed with that of a ferric salt, a precipitate of *Prussian blue* is obtained. Prussian blue is used in dyeing and calico printing, and in making bluing and blue ink.

Potassium ferricyanid, $K_3Fe(CN)_6$ (*red prussiate of potash*), is formed from a solution of the yellow prussiate by the action of chlorin or bromin. It is an important constituent of blue-print paper.

NICKEL

437. Occurrence and Preparation. Nickel, like iron, never occurs free except in meteorites. Its chief ore is *garnierite*, a complex silicate which is found in large quantities in New Caledonia. Nickel is obtained from this ore by a blast-furnace process similar to that used in obtaining iron. It is also obtained by electrolytic processes.

438. Properties. *Physical.* (Table I., Appendix *D*.) Nickel is almost as white as silver, has a brilliant luster, and is feebly magnetic. It is very tough and hard and may be welded like iron.

Chemical. Nickel is not affected by the air, is acted on only slowly by hydrochloric and sulfuric acids, but is rapidly dissolved by nitric acid.

439. Uses. Nickel is employed in nickel-plating, and as a constituent of several important alloys. German silver contains two parts of copper and one each of nickel and zinc. A nickel five-cent piece contains one part of nickel to three of copper. Its alloys with steel (nickel steel) are characterized by great hardness, toughness, and durability, and for this reason are used in making armor plate.

440. Some Nickel Compounds. The *chlorid*, $NiCl_2$, *nitrate*, $Ni(NO_3)_2$, and *sulfate*, $NiSO_4$, are green, soluble salts made by dissolving the metal, its oxid or hydroxid, in the respective acids. The *hydroxid*, $Ni(OH)_2$, is thrown down from solutions of nickel salts by the addition of an alkali, as a voluminous, apple-green precipitate, which, when heated, loses water and is converted into *nickel oxid*, NiO, a green powder. *Nickel sulfid*, NiS, forms a black precipitate when a soluble sulfid is added to

a solution of a nickel salt. *Nickel carbonyl*, $Ni(CO)_4$, is prepared by passing carbon monoxid over finely divided nickel; it is a colorless, strongly refracting, combustible liquid, which boils at 43°. A method of extracting nickel from low-grade ores is based on the formation of nickel carbonyl.

COBALT

441. Cobalt. Cobalt is a rare element found associated with nickel, to which it bears a close resemblance. Cobalt salts are blue when dry, and red when dissolved in water. A solution of *cobaltous chlorid*, $CoCl_2$, makes a good sympathetic ink. *Smalt*, a silicate of cobalt, imparts to glass a beautiful blue color.

Exercises

1. What is the object of painting all structural iron?

2. Both iron and aluminum become coated with their respective oxids when exposed to the air. Why is it that the iron gradually is entirely "eaten up by the rust" while the aluminum is not perceptibly changed?

3. What is the soluble product of the action of (*a*) hydrochloric acid and (*b*) sulfuric acid on ferrous sulfid?

4. What objections are there to the use of iron pyrites as an ore of iron?

5. Does tinned iron rust? Does galvanized iron rust? How can you account for the difference in the behavior of the metallic coatings?

Problems

1. Compute which has the larger percentage of iron, hematite, Fe_2O_3, or magnetite, Fe_3O_4.

2. Iron oxid, Fe_2O_3, contains 70 per cent of iron and 30 per cent of oxygen. If the atomic weight of oxygen is 16.00, what is that of iron?

3. How many grams of ferrous sulfid are needed to form enough hydrogen sulfid to precipitate 100 g. of copper sulfate?

4. Maumené, in 1850, reduced 12.5120 g. of iron oxid, Fe_2O_3, by heating it in a current of hydrogen and obtained 8.7585 g. of iron ; calculate its atomic weight. How much water was formed in this determination ?

5. Berzelius, in 1844, dissolved 2.9993 g. of iron in nitric acid and heated the nitrate formed until it was converted in ferric oxid, Fe_2O_3 ; 4.2835 g. of the oxid were obtained. Find the atomic weight of iron.

6. Baubigny, in 1883, obtained by heating 11.7540 g. of nickel sulfate, $NiSO_4$, 5.1920 g. of nickel oxid. The atomic weights of oxygen and sulfur are 16.00 and 32.06 ; what is the atomic weight of nickel ?

7. Russell, in 1869, found on dissolving nickel in hydrochloric acid that the weight of the hydrogen was 3.411 per cent. of the weight of the nickel. Calculate the atomic weight of nickel.

8. Russell, in 1863, reduced 28.5943 g. of nickel oxid by heating in hydrogen and obtained 22.5943 g. of nickel. What is the atomic weight of nickel ?

9. Russell, in 1869, found that the amount of hydrogen evolved by dissolving cobalt in hydrochloric acid was 3.4017 per cent of the metal. Calculate the atomic weight of cobalt.

SVANTE ARRHENIUS

1859 —— ; Swede

*Originator of the Theory of Elec-
trolytic Dissociation, and con-
tributor to the Modern Theory
of Solutions*

JACOBUS HENRICUS VAN'T HOFF

1802 —— ; Dutch

*Applied the gas laws to solutions.
Studied the equilibrium relation-
ships of solutions. Founder of
Modern Theory of Solutions*

WILHELM OSTWALD

1853 ——; German

*Ardent advocate of the Modern
Theory of Solutions, many im-
portant deductions from which
he has drawn*

Plate VII

ARRHENIUS

OSTWALD   VAN'T HOFF

Plate VII

CHROMIUM AND MANGANESE

CHROMIUM

442. Occurrence and Preparation. Chromium, a rather rare element, never occurs free, and is principally found in *chromite*, $FeO \cdot Cr_2O_3$ (*chrome iron stone*), and in *crocoisite*, $PbCrO_4$ (lead chromate). It is prepared by fusing chromite with potassium hydroxid, thus forming potassium chromate, from which chromic oxid, Cr_2O_3, may be obtained. This can be reduced by heating it with charcoal in an electric furnace or by the action of aluminum.

443. Properties. *Physical.* (Table I., Appendix *D.*) Chromium is a lustrous metal which takes a fine polish. It is very hard and is infusible except at the temperature of the electric arc. It is used in the manufacture of a very hard steel, called *chrome steel*, which is made into armor plate, projectiles, safes, and other articles that require great power of resistance.

Chemical. Nickel is unaffected by the air. It forms three sets of compounds; in the *chromous* and *chromic* compounds it acts as a base, while in the *chromates* it behaves as an acid-forming element, resembling sulfur in this particular.

444. The chromous compounds have a great tendency to become oxidized into the chromic compounds, and can be prepared and preserved only

[321]

when not in contact with air. In these compounds the chromium is bivalent, as chromous oxid, CrO, chromous chlorid, $CrCl_2$

445. Chromic Compounds. *Chromic hydroxid*, $Cr(OH)_3$, is formed as a green precipitate when an alkalin hydroxid is added to a solution of a chromic salt. When heated, it loses water and is converted into chromic oxid, Cr_2O_3, a green solid, which may also be prepared by heating ammonium chromate. When fused with silicates, it colors them green, and hence is used for coloring glass and china.

Chromic sulfate, $Cr_2(SO_4)_3$, and *chromic chlorid*, $CrCl_3$, are violet solids when dry, which form green solutions from which green crystals containing water of crystallization may be obtained.

Chrome alum, $Cr_2(SO_4)_3 \cdot K_2SO_4 + 24\,H_2O$, is prepared by passing sulfur dioxid into a solution of potassium dichromate containing free sulfuric acid:

$$K_2Cr_2O_7 + H_2SO_4 + 3\,SO_2 \rightarrow K_2SO_4 \cdot Cr_2(SO_4)_3 + H_2O$$
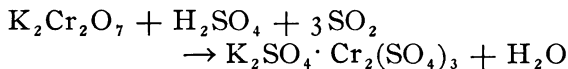
It forms large violet crystals, and is used in tanning and dyeing.

446. Chromates. There are numerous salts of the type M_2CrO_4, which are derived from the oxid CrO_3, chromic anhydrid. The corresponding acid has not as yet been isolated. The salts of chromic acid are analogous to those of sulfuric acid.

Chromic anhydrid is obtained by the action of sulfuric acid on a strong solution of potassium dichromate, $K_2Cr_2O_7$, and forms long, red, needle-like crystals which are very soluble in water. When heated to 250° it decomposes into chromic oxid and

water. It is so powerful an oxidizing agent that its solution cannot be filtered through paper, which is destroyed by oxidation.

The *alkali chromates* are prepared by fusing chromate with an alkalin carbonate and extraction with water. *Potassium chromate* forms yellow crystals.

The bichromates are regarded as compounds of a chromate with chromic anhydrid:

$$K_2CrO_4 + CrO_3 \rightarrow K_2Cr_2O_7$$

They are prepared by adding sulfuric acid to a solution of the chromate.

Potassium dichromate is a red, soluble salt, frequently used as an oxidizing agent; it is reduced to chromic sulfate when heated with sulfuric acid; the sulfate of potassium also is formed, and some of the oxygen is made available for oxidation.

LEAD CHROMATE, $PbCrO_4$, is a yellow solid, formed when potassium chromate or dichromate is added to a solution of a lead salt. It is used under the name of *chrome yellow* as the base of yellow paint.

MOLYBDENUM, TUNGSTEN, AND URANIUM are rare metals related to chromium. Tungsten is used to harden steel, ammonium molybdate, $(NH_4)_2 MoO_4$, is used in the analysis of phosphorus in compounds; and some of the salts of uranium when fused with glass cause it to appear yellow by reflected light, and green by transmitted light.

MANGANESE

447. Occurrence and Preparation. Manganese is widely diffused in nature, never occurring free, however, but in combination as oxid, MnO_2 (*pyrolusite*), and Mn_3O_4 (*hausmannite*), or carbonate, $MnCO_3$ (*rhodochrasite*). It is prepared by reducing pyrolusite in an electric furnace.

448. Properties. (Table I., Appendix D.) Manganese is very lustrous and undergoes a superficial oxidation so that it has an iridescent sheen. It is very hard and infusible. Alloys of manganese and iron (spiegel iron and ferro manganese) are extensively used in the manufacture of steel. When finely divided, manganese decomposes boiling water, and it is soluble in acids, forming manganous salts.

449. Manganese Compounds. Manganese forms several series of compounds, as manganous oxid, MnO, manganic oxid, Mn_2O_3, manganic acid, regarded as derived from an anhydrid, MnO_3, and permanganic acid, $HMnO_4$, derivable from the oxid, Mn_2O_7. In some way the compounds of manganese, especially the salts, resemble the corresponding compounds of iron.

450. Oxids. The following oxids are known: *Manganous oxid*, MnO, a green powder, oxidizing readily to the higher oxid, Mn_3O_4; manganic oxid, Mn_2O_3, a dark brown powder; *mangano-manganic oxid*, Mn_3O_4 or $MnO \cdot Mn_2O_3$, a brownish-red powder; *manganese dioxid*, MnO_2, a black solid (pyrolusite); and *manganese heptoxid*, Mn_2O_7, a dark-colored liquid. The only important one is the dioxid, which is used in making chlorin and oxygen, in decolorizing glass, and in manufacturing steel.

451. Manganous Salts. The salts are pink in color, soluble in water, and behave like those of magnesium and iron. *Manganous sulfid*, MnS, is a flesh-colored precipitate formed when ammonium sulfid is added to a solution of a manganous salt, as the chlorid, $MnCl_2$, or sulfate, $MnSO_4$.

452. Manganates and Permanganates. When manganese compounds are fused with potassium hydroxid in the presence of air, or better, of some oxidizing agent, as potassium nitrate or chlorate, a green mass results, which forms a dark-green solution of *potassium manganate*, K_2MnO_4. When this solution is boiled and carbon dioxid or chlorin passed into it, potassium permanganate, $KMnO_4$, is formed.

$$3\,K_2MnO_4 + 2\,CO_2 \rightarrow 2\,K_2CO_3 + 2\,KMnO_4 + MnO_2$$
$$2\,K_2MnO_4 + Cl_2 \rightarrow 2\,KCl + 2\,KMnO_4$$
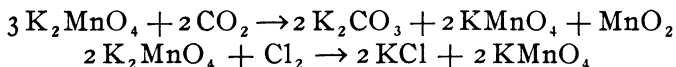
Potassium permanganate forms hard, greenish-black crystals, which dissolve in water to form a deep purple solution. This solution acts as a powerful oxidizing agent, and is used on a large scale to purify water and sewage. It is also used in medicine, in bleaching and dyeing, and in staining wood.

Problems

1. Ramson, in 1889, heated 6.65949$g.$ of ammonium dichromate, $(NH_4)_2Cr_2O_7$, and obtained 4.01871$g.$ of chromium trioxid, Cr_2O_3. Taking the atomic weights of nitrogen, hydrogen, and oxygen as 14.041, 1.008, and 16.000, respectively, calculate the atomic weight of chromium.

2. Siewert, in 1861, found that 7.6919$g.$ of silver chlorid were obtained by the action of silver nitrate on a solution containing 2.8338$g.$ of chromium chlorid, $CrCl_3$. Knowing that the atomic weights of silver and chlorin are 35.45 and 107.94, respectively, what is that of chromium?

3. Marignac, in 1884, converted 10.6647$g.$ of manganous oxid, MnO, into 22.6875$g.$ of manganous sulfate, $MnSO_4$. Taking the atomic weights of sulfur as 32.06, and of oxygen as 16.00, find the atomic weight of manganese.

CHAPTER XXXI

THE PERIODIC SYSTEM

453. Retrospect. In our foregoing study of the elements we have found that they could be classed into groups, the members of which were similar as regards their valence, physical properties, and chemical behavior. We found also that in the case of certain groups of three elements there was a simple relationship between their atomic weights, for the half of the sum of the smallest and largest atomic weight equaled the intermediate atomic weight (page 198). In 1865, Newlands, an Englishman, proposed his Law of Octaves; he had found that if the elements are arranged in the order of their atomic weights, the eighth, fifteenth, etc., elements exhibited properties similar to those of the first element. And about five years later, the Russian, Mendeleeff, and the German, Lothar Meyer, independently extended these observations and arrived at conclusions embraced by the term "Periodic Law."

454. Development of the System. If we write the symbols of the elements in the order of their increasing atomic weights, beginning with lithium and ending with chlorin, we have:

Li, 7; Be, 9; B, 11; C, 12;   N, 14; O, 16; F, 19
Na, 23; Mg, 24; Al, 27; Si, 28.4; P, 31 ; S, 32; Cl, 35.5

We see that while there is a gradual change in the properties of the elements in the same horizontal

line, there is a sudden change in passing from the end of the first line to the beginning of the second; fluorin and sodium have opposite properties. We note, moreover, that the elements in the same vertical columns exhibit close similarities, and indeed are members of the groups of elements we have been studying.

The regular gradation of such properties as valence and specific gravity is shown in the following table:

Element	Na	Mg	Al	Si	P(*red*)	S	Cl(*liq*.)
Valence	I.	II.	III.	IV.	(V. & VII.)	(II. IV. & VI.)	(I. & VII.)
Sp. Grav.	0.97	1.75	2.67	2.49	2.14	2.06	1.33

Furthermore, if we write down the symbols of a series of elements according to their increasing atomic weights, beginning with another univalent metal, as silver, for instance, and placing the atomic weights and specific gravities under the symbols, we have:

	Ag'	Cd''	Zn'''	Sn''''	Sb'''	Te''	I'
Atom. Wt.	108	112.4	114	118.5	120	127	126.9
Sp. Grav.	10.5	8.6	7.4	7.2	6.7	6.2	4.9

Reading from left to right we see a regular change of properties, and if this series be written down below the two preceding ones we have:

Li, 7;   Be, 9.1;   B, 11;   C, 12;   N, 14;   O, 16;   F, 19
Na, 23;   Mg, 24.4;   Al, 27.1; Si, 28.4;   P, 31;   S, 32;   Cl, 35.5
Ag, 108 ; Cd, 112.4 ; Zn, 114 ; Sn, 118.5 ; Sb, 120 ; Te, 127 ; I, 126.9

We observe that the elements in the same vertical column belong to a natural group, as that of the alkali metals or the halogens.

These and other facts lead to the conclusion that the properties of the elements stand in a close

relationship to their atomic weights. Moreover, there are in the series regular recurrences of elements of similar properties at intervals of about 16. In the language of mathematics, when one quantity stands in such a relationship to another that when one changes the other also changes, the one is said to be a *function* of the other, and when as one quantity increases uniformly the other assumes at regular intervals the same value, the function is said to be a *periodic* one. Borrowing then this mode of expression we may say:

The properties of the elements are periodic functions of their atomic weights. This statement is known as the Periodic Law. The arrangement of the elements in these periods is shown in the table opposite.

455. Large and Small Periods. In the period beginning with potassium, it is seen that after manganese, the seventh member, there occur three quite similar elements, iron, nickel, and cobalt, which do not fit under potassium, calcium, and scandium. In order to have the next period, which begins with copper, correspond with the preceding period, it is necessary to place iron, nickel, and cobalt in an intermediate group by themselves. After the first two periods of seven elements each, comes one of seventeen elements, made up of two small periods of seven elements each and three elements intermediate. A similar long period occurs also farther on in the table.

456. The Value of the Periodic Law consists in the following facts:

I.   It gives a systematic classification of the elements, which is nearly free from arbitrariness.

MENDELÉEFF'S TABLE (*With the Atomic Weights in Round Numbers*)

GROUP	I	II	III	IV	V	VI	VII	VIII	O
Type of the Compounds: With hydrogen or a halogen;	MX	MX_2	MX_3	MX_4	MX_3	MX_2	MX		
With oxygen (highest stage)	M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_3 MO_2 MO	
First Period Row 1							H 1		He 4
2	Li 7	Be 9.1	B 11	C 12	N 14	O 16	F 19		Ne 20
Second „ 3	Na 23	Mg 24.4	Al 27.1	Si 28.4	P 31.0	S 32	Cl 35.4		Ar 40
Third „ 4	K 39	Ca 40	Sc 44.1	Ti 48.1	V 51.2	Cr 52.1	Mn 55.0	Fe 56.0 Co 59.0 Ni 58.7	Kr 81.6
„ 5	Cu 63.6	Zn 65.4	Ga 70	Ge 72	As 75	Se 79.1	Br 80		—
Fourth „ 6	Rb 85.4	Sr 87.6	Y 89	Zr 90.7	Nb 94	Mo 96.0	— 100	Ru 101.7 Rh 103.0 Pd 106	X 128
„ 7	Ag 108	Cd 112.4	In 114	Sn 118.5	Sb 120	Te 127	I 126.9		
„ „ 8	Cs 133	Ba 137.4	La 138	Ce 140	(Di 142)?	—	Sa 150	—	—
„ „ 9	—	—	Yb 173	Er 166	—	—	—	—	
„ „ 10	—	—	—	—	Ta 183	W 184	—	—	
„ „ 11	Au 197.2	Hg 200.3	Tl 204.1	Pb 206.9	Bi 208.5	—	—	Os 191 Ir 193.0 Pt 194.8	
„ 12	—	—	—	Th 232.5	—	Ur 239.5	—		

2. It assists in the fixing of the atomic weights of such elements, only the equivalent weights of which can be determined.

3. It furnishes a means of predicting the properties of elements as yet not discovered.

4. It may be employed to confirm or correct the atomic weights of elements which may be doubtful.

Illustrations of the second and third items of value of the law are too difficult for an elementary book, but it may be stated that they have been applied in several cases with complete success.

457. Classification of the Elements. The physical and chemical properties of an element may be ascertained from the position it occupies in the system and particularly by the four adjacent elements, its *analogues*. Thus, if the properties of magnesium were unknown, they could be deduced approximately from those of its four analogues — sodium, beryllium, aluminum, and calcium. For instance, its atomic weight is very nearly the average of the atomic weights of its analogues.

$$\frac{23 + 9 + 27 + 40}{4} = 24.75$$

Also, its specific gravity, by experiment found to be 1.75, is about the average of the specific gravities of its analogues:

$$\frac{0.97 + 2.10 + 2.56 + 1.58}{4} = 1.80$$

458. Prediction of Unknown Elements. The blanks or gaps in the table represent the positions of elements as yet undiscovered. When the table

was first drawn up, the number of blanks was greater than now, and Mendeleeff did not hesitate to prophesy the existence of elements to fill the gaps, and even predicted the properties which they should possess. His predictions have been fulfilled in several cases. The three elements, gallium, germanium, and scandium, have all been discovered since his formulation of the law, and have been found not only to naturally fall into the places he had assigned them, but also to present very closely the physical and chemical properties he had predicted for them. The filling up of all the gaps now present in the table is probably but a matter of time. It should be stated, however, that the system did not in the least lead chemists to suspect the existence of the elements, helium and argon, to which, indeed, it is found difficult to assign satisfactory places in the table. The system certainly has faults, but is full of suggestions, the following up of which has led to important discoveries. The formulation of the Periodic Law has been a decided help to the advance of chemical knowledge, and undoubtedly paves the way towards a deeper insight into the nature and relationships of the different kinds of matter, if not into the nature of matter itself.

CHAPTER XXXII

SOME COMMON ORGANIC COMPOUNDS

The distinction between organic chemistry and inorganic chemistry has already been made clear (§ 100). Since many of the compounds of carbon are in everyday use, mention of their occurrence, preparation, and properties will be made in the following pages, although nothing like a thorough-going and systematic treatment will be attempted.

459. Composition of Carbon Compounds. Although the number of compounds of carbon is greater than the number of compounds of all the other elements, yet comparatively few elements are combined with carbon to form the majority of these compounds. Hydrogen, oxygen, and nitrogen are the most frequently occurring elements in carbon compounds as they occur in nature, although phosphorus and sulfur are not uncommon. Carbon compounds made in the laboratory may contain any element; the halogens are especially common.

460. The Valency of Carbon; Graphic Formulas. Carbon is quadrivalent in most of its compounds; carbon monoxid, in which it is bivalent, is a familiar exception. The quadrivalency of carbon is the corner stone of the edifice of organic chemistry.

It is customary to bring out the valencies of elements by writing their symbols in connection with dashes equal in number to their valence. Thus:

$$-\overset{|}{\underset{|}{C}}- \qquad -\overset{}{\underset{|}{N}}- \qquad -O- \qquad H-$$

The formulas of methane, ammonia, water, and hydrogen expressed accordingly are:

$$\overset{H}{\underset{H}{\overset{|}{H-C-H}}} \qquad \overset{}{\underset{H}{\overset{}{H-N-H}}} \qquad H-O-H \qquad H-H$$
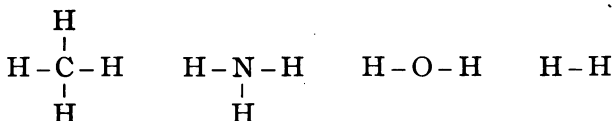
The formulas of the two first chlorin substitution products of methane (page 171) are

$$\overset{H}{\underset{H}{\overset{|}{H-C-Cl}}} \qquad\qquad \overset{H}{\underset{Cl}{\overset{|}{H-C-Cl}}}$$

(methyl chlorid)   *(methylene chlorid)*
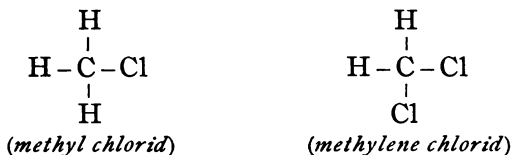
461. The Nature of Carbon. The large number of carbon compounds is due chiefly to the valency of carbon and its behavior toward itself. This behavior may be summed up in the following statements:

1. Several carbon atoms may be joined by one, two, or three valencies, as $C-C$, $C=C$, $C\equiv C$.

2. Several carbon atoms may unite so as to form the so-called "carbon chains," as $C-C-C-C$, $C-C-C=C-C$, $C=C-C-C$. The number of atoms thus linked together has been found to be as large as thirty.

3. The "carbon chains" may be *open* or *closed*. Open chains have separate atoms at each end, as shown in *2*, while in the closed chains those atoms

which would be the first and the last atoms in the closed chain unite so as to form a ring, thus:

$$\begin{array}{ccc}
& \diagup C \diagdown \\
C & & C \\
| & & | \\
C & & C \\
& \diagdown C \diagup
\end{array}
\qquad
\begin{array}{c}
\diagup C \diagdown \\
C - C
\end{array}
\qquad
\begin{array}{ccccc}
& \diagup C \diagdown & & \diagup C \diagdown \\
C & & C & & C \\
| & & | & & | \\
C & & C & & C \\
& \diagdown C \diagup & & \diagdown C \diagup
\end{array}$$
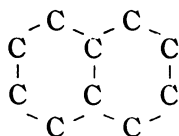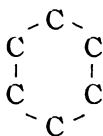
4. Molecules of carbon compounds may contain both open and closed chains:

$$\begin{array}{ccc}
& \diagup C \diagdown & \diagup C - C \\
C & & C \\
| & & | \\
C & & C - C - C - C \\
& \diagdown C \diagup
\end{array}
\qquad
\begin{array}{ccc}
& \diagup C \diagdown & \diagup C \\
C & & C \\
| & & | \\
C & & C - C - C \\
& \diagdown C \diagup
\end{array}$$
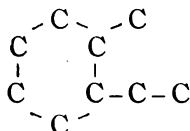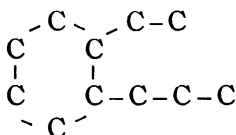
5. Other elements, excepting, of course, univalent elements, may take part in the formation of both open and closed chains:

$$\begin{array}{c}
C - C \diagdown \\
\qquad N - \\
C - C \diagup
\end{array}
\qquad
\begin{array}{c}
C - C \diagdown \\
| \qquad S \\
C - C \diagup
\end{array}
\qquad
\begin{array}{c}
\diagup C - C \diagdown \\
C \qquad\qquad N - \\
\diagdown C - C \diagup
\end{array}$$
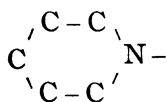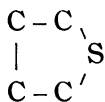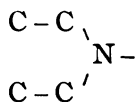
462. Radicals. We have learned (§ 135) that there are certain groups of atoms which are found repeating themselves in numerous compounds derived from one another and which play in these compounds the part of an atom. For instance, *methyl*, $-CH_3$, and *methylene*, $=CH_2$, in the formulas on page 333, are simple and common radicals. They have never been isolated; all attempts at isolation have resulted in the formation of the compounds $H_3C - CH_3$ (*ethane*, C_2H_6) and $H_2C - CH_2$ (*ethylene* C_2H_4).

463. Isomerism and Polymerism. Ethane and ethylene have molecular weights twice as large as methyl and methylene. Methyl and methylene are said to *polymerize* and form ethane and ethylene; and methyl and ethane, and methylene and ethylene are said to be *polymers* of each other. Polymers then are substances which have the same percentage composition, but different molecular weights and properties.

There are also many substances which have the same percentage composition and the same molecular weight, but which have quite different properties. Their molecules are made of equal numbers of the same atoms. The differences in properties then must be due to differences in the arrangement of the atoms in the molecule. Such compounds are called *isomers*.

464. Classification of Carbon Compounds. Only the most common of the numerous classes of compounds of carbon can be mentioned here, such as (1) hydrocarbons, (2) alcohols, (3) aldehydes, (4) ethers, (5) acids, (6) esters, (7) carbohydrates, (8) benzene derivatives.

HYDROCARBONS

Hydrocarbons have already been considered in Chapter IX. Some additional ones will be discussed under *Benzene Derivatives* (§ 487).

ALCOHOLS

The alcohols may be regarded as hydroxids of certain radicals, such as methyl and ethyl. They behave like bases in that they combine with acids, with elimination of water, to form compounds

analogous to salts in constitution; the latter compounds are termed esters or ethereal salts.

465. Methyl Alcohol, CH_3OH. Methyl alcohol is one of the products of the dry distillation of wood, and for that reason is often called *wood alcohol* or *wood spirit*. It is a colorless liquid with a spirituous odor and burning taste. It mixes with water in all proportions. It is used as a solvent for oils, fats, and shellac, and in the manufacture of varnishes.

466. Ethyl Alcohol, C_2H_5OH. Ethyl alcohol is prepared by the action of yeast on a solution containing glucose; carbon dioxid (§ 89) is the other main product. The reaction during fermentation may be represented by the equation:

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2$$
$$\text{(\textit{glucose})} \qquad \text{(\textit{alcohol})} \qquad \text{(\textit{carbon dioxid})}$$
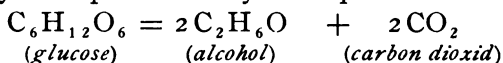
When the fermenting solution contains something over 10 per cent of alcohol, the fermentation ceases, *i. e.*, the yeast plant stops multiplying. The solution is then filtered and concentrated by distillation.

Ethyl alcohol is a colorless liquid, having a spirituous odor and a burning taste. It is miscible in all proportions with water. The ordinary commercial article contains from 5 to 10 per cent of water; *proof spirit* contains 50 per cent of water. *Pure* or *absolute alcohol* is prepared by distilling ordinary alcohol over lime or calcium carbid to remove the water.

As alcohol is a good solvent for most oils, gums, and resins, it is extensively used in the manufacture of essences, extracts, tinctures, varnishes, and medicines. It is employed as an antiseptic, as a source

of heat in alcohol lamps, and as a preservative for anatomical specimens in museums. It is often converted into vinegar (§ 473), and many organic compounds require its use in their preparation.

467. Alcoholic Liquors. The juices of fruits when exposed to the air receive ferments (fungi capable of producing fermentation) from it and, if the conditions are right, go through the process of fermentation. This fermented juice forms *wine*. Grain also when soaked in water containing malt (barley which has sprouted) undergoes fermentation, and, when hops are added to the fermented liquor, *beer* is the product. Wine and beer then are for the most part mixtures of alcohol and water, but with numerous other substances present which give each liquor its peculiar properties. Beer contains from 3 to 7 per cent of alcohol; wine from 6 to 20 per cent.

When wine is distilled the distillate is known as *brandy*. Likewise, the distillation of the liquors in which the fermentation of substances such as grain or molasses has taken place, yields other *distilled liquors*, such as whisky, gin, or rum.

468. Glycerin, $C_3H_5(OH)_3$. While ethyl and methyl alcohols contain but one hydroxyl group, glycerin contains three, so that its chemical behavior is correspondingly complex. The method of preparation of glycerin will be described under *Soap* (§ 480).

Glycerin is a thick, colorless, odorless liquid with a sweet taste. It is miscible with both water and alcohol, and absorbs moisture from the air. It is used in the manufacture of copying inks, toilet

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soaps, printers' ink rollers, and nitroglycerin; it is also used as a solvent, a lubricator, a cosmetic, as sweetening in certain liquors, preserves, and candy, and as an adulterant for molasses.

ALDEHYDES

When alcohols are oxidized under certain conditions, aldehydes are formed; these may be regarded as compounds of the aldehyde radical, CHO, with other organic radicals.

469. Formaldehyde, HCHO. Formaldehyde is a gas with a penetrating odor; it is readily soluble in water. It is used extensively as a disinfectant and a food preservative. A solution containing 40 per cent of formaldehyde is known as *formalin*.

470. Acetaldehyde, CH_3CHO. Acetaldehyde is obtained by partially oxidizing alcohol.

$$C_2H_5OH + O = CH_3CHO + H_2O$$
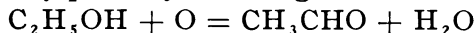
It is a colorless liquid with a suffocating odor. It is a powerful reducing agent, and is sometimes used to precipitate silver as a coating on glass in making mirrors.

When alcohol is oxidized with chlorin, *chloral*, CCl_3CHO, is produced. Chloral forms with water *chloral hydrate*, $CCl_3CHO \cdot H_2O$, a compound often used to ease pain and induce sleep. Chloral in alkalin solution forms *chloroform*, $CHCl_3$, the well-known anæsthetic. *Iodoform*, CHI_3, which is the iodin compound corresponding to chloroform, is a yellow solid with a disagreeable odor. It is used as a surgical dressing.

NOTE. The word aldehyde is intended to show that *al*cohol is *dehyd*rogenated to produce it. The prefix *acet* indicates that *acet*-aldehyde when oxidized yields *acet*ic acid.

ETHERS

Ethers may be regarded as oxids of hydrocarbon radicals. They are prepared by removing one molecule of water from two molecules of an alcohol.

471. Ethyl Ether, $(C_2H_5)_2O$. Ethyl ether is prepared by heating alcohol with the dehydrating agent, concentrated sulfuric acid:

$$\begin{array}{l} C_2H_5\ OH \\ C_2H_5\ OH \end{array} - H_2O \rightarrow \begin{array}{l} C_2H_5 \\ C_2H_5 \end{array}\!\!> O$$
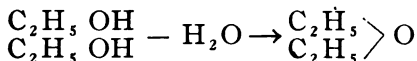
Ether is a colorless liquid with a peculiar and rather pleasant taste and odor. It is very volatile and as its vapor is very inflammable, it should not be brought near a flame. It is miscible with water only to a limited extent. Its chief use is as an anæsthetic.

ACIDS

Organic acids are compounds of certain organic radicals with *carboxyl*, CO_2H. They may be prepared by oxidation of the corresponding alcohols.

$$\begin{array}{cccc}
\text{H} & \text{H} & \text{H} & \\
| & | & | & \\
\text{H} - \text{C} - \text{H} & \text{H} - \text{C} - \text{OH} & \text{C} = \text{O} & \text{O} = \text{C} - \text{O} - \text{H} \\
| & | & | & | \\
\text{H} - \text{C} - \text{H} & \text{H} - \text{C} - \text{H} & \text{H} - \text{C} - \text{H} & \text{H} - \text{C} - \text{H} \\
| & | & | & | \\
\text{H} & \text{H} & \text{H} & \text{H} \\
(ethane) & (ethyl\ alcohol) & (acetaldehyde) & (acetic\ acid)
\end{array}$$
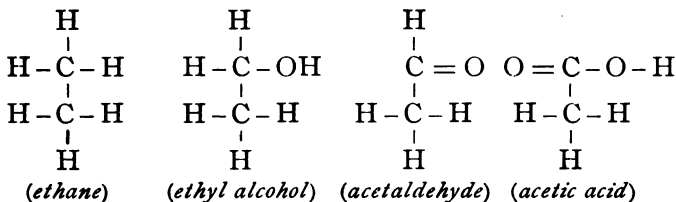
472. Acetic Acid, CH_2CO_2H. Acetic acid is one of the products of the destructive distillation of wood. The distillate (called *pyroligneous acid*) is a dark red liquid containing about 10 per cent of acetic acid, together with smaller proportions of methyl alcohol and numerous other organic compounds. When this acid distillate is neutralized

with lime or soda, calcium or sodium acetate is
formed. This is then heated with sulfuric acid;
acetic acid is thus freed from the base and collects
as a distillate mixed with about 70 per cent of
water. By expelling the water of crystallization
from sodium acetate before distilling it with sul-
furic acid, a very concentrated acetic acid is ob-
tained; this is ·called *glacial acetic acid* because it
solidifies at 17°.   .

Acetic acid is a colorless liquid with a pungent
odor and sharp taste. It is miscible in all propor-
tions with water.

ACETATES. *Acetic acid* is monobasic and forms the
series of salts known as *acetates*, some of which are
important.

Sodium acetate, $NaC_2H_3O_2 + 3H_2O$, forms white
crystals. It is used in the manufacture of pure acetic
acid and in making certain dyes.

Lead acetate, $Pb(C_2H_3O_2)_2$, is a white solid used in
dyeing and in making a yellow paint.

Aluminum acetate, although not known in a state of
purity, is used in an impure state when in solution
(known as "red liquor") for dyeing and calico printing.

Iron acetate is used in solution in dyeing silks and
cottons black. The solution is black and is known as
"iron liquor."

Verdigris is a complex copper acetate used in manu-
facturing blue paint.

Paris green is another complex acetate of copper
and arsenic (page 248).

473. Vinegar. Vinegar is dilute, impure acetic
acid, prepared by the oxidation of weak alcohol.
The oxidation is effected by fermentation. Thus,
cider, beer, and weak wines become sour when
exposed to the air in a warm place, because a certain
ferment flourishes in them, changing the alcohol to

acid. Strong wine and pure dilute alcohol do not sour, because the ferment cannot grow in them.

Vinegar is manufactured by soaking wood shavings in vinegar ferment, placing them in a cask with numerous holes punched in it so as to give free access to the air, and allowing dilute wine, cider, or alcohol to trickle down over them. The ferment acts rapidly upon the alcohol thus spread out over the shavings, and the liquor after two or three such treatments is converted into vinegar.

474. Oxalic Acid, $C_2H_2O_4 + 2H_2O$. Oxalic acid, combined with calcium, occurs in rhubarb and sorrel. It is manufactured by heating sawdust and caustic potash together, and treating the residue with lime. The calcium salt is then decomposed by heating with sulfuric acid.

Oxalic acid forms white, soluble crystals, which are very poisonous. Its use in removing ink spots and iron rust from clothing is well known. The acid and its salts are also extensively employed in dyeing, calico printing, photography, and in the manufacture of dyes.

475. Lactic Acid, $C_3H_6O_3$. Lactic acid is a product of the fermentation of milk sugar, and is hence found in sour milk. It forms a thick, sour liquid, readily decomposed by heat. Lactic acid and some of its salts are used in medicine, and in dyeing and calico printing.

476. Tartaric Acid, $C_4H_6O_6$. The potassium salt of tartaric acid occurs in grapes and other fruits. When grape juice ferments, this acid potassium tartrate separates from its solution and collects on the bottom of the casks. This crude *tartar* or *argol*

is converted into pure tartaric acid by treating it with chalk and then with sulfuric acid. Tartaric acid forms large, transparent crystals, soluble in both water and alcohol. It is the acid ingredient of a Seidlitz powder, the other being sodium bicarbonate.

When acid potassium tartrate is purified, it is known as *cream of tartar*, and is used in making *baking powder* (page 195). *Tartar emetic* is a tartrate of potassium and antimony; it is used in medicine.

MALIC ACID, $C_4H_6O_5$. Malic acid is found free and in the form of salts in many fruits. It is a white, crystalline solid, soluble in water.

CITRIC ACID, $C_6H_8O_7$. Citric acid occurs free in lemons and oranges, and in a much smaller quantity in currants and gooseberries. It forms white crystals, readily soluble in water. It gives the sour taste to lemonade, and its salt, magnesium citrate, is used in medicine.

BUTYRIC ACID. Butyric acid is found in rancid butter. It is a thick liquid with a disagreeable odor.

OLEIC ACID, $C_{18}H_{34}O_2$, *stearic acid*, $C_{18}H_{36}O_2$, and *palmitic acid*, $C_{16}H_{32}O_2$, occur in combination with glycerin to form most of the natural fats and oils. The acids are white solids at low temperatures.

ESTERS

477. Formation. The hydrogen in the carboxyl of an organic acid may be replaced by an alcohol radical, just as inorganic acids and bases unite in neutralization (§ 181); the products are water and *esters* or *ethereal salts*. As the water which is formed may interfere with the reaction, concentrated sulfuric acid is used to absorb the water. Thus, when a mixture of ethyl alcohol, acetic acid, and sulfuric acid is warmed, *ethyl acetate* is formed:

$$C_2H_5OH + CH_3CO_2H \rightarrow CH_3CO_2C_2H_5 + H_2O$$
(ethyl acetate)
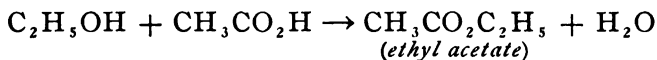
The analogy between this reaction and the reaction between sodium hydroxid and acetic acid is manifest:

$$NaOH + CH_3CO_2H \rightarrow NaCH_3CO_2 + H_2O$$
(sodium acetate)
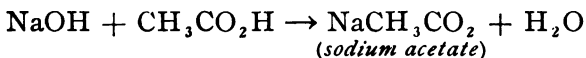
478. Properties of Esters. Many esters are found in fruits and flowers, often giving to them their characteristic flavor and fragrance. Some are prepared by artificial means and used as cheap substitutes for more expensive flavors in extracts, perfumery, and beverages. Thus, *ethyl butyrate*, the ester of ethyl alcohol and butyric acid, has the taste and fragrance of pineapples, *amyl acetate* that of bananas, and *amyl valerate* that of apples.

479. Fats and Oils. Most animal and vegetable fats and oils, such as suet, tallow, butter, palm and olive oils, consist almost entirely of mixtures of glycerin esters or ethers of oleic, stearic, and palmitic acids. For brevity these esters are termed *olein*, $C_3H_5(OC_{18}H_{33}O)_3$, *stearin*, $C_3H_5(OC_{18}H_{35}O)_3$, and *palmitin*, $C_3H_5(OC_{16}H_{31}O)_3$. As olein is liquid and palmitin and stearin solid at ordinary temperatures, the consistence of a fat or oil depends on relative proportions of their three constituents.

If the fats or oils are treated with sulfuric acid or heated with very hot steam, they break up into the free acids and glycerin; if they are boiled with a caustic alkali solution, glycerin is freed, and alkalin salts of the acids are formed. The fats are said to be *saponified*, and the process is called *saponification*. Thus, if stearin be boiled with sodium

hydroxid solution, the change represented by the following equation takes place:

$$C_3H_5(OC_{18}H_{35}O)_3 + 3\,NaOH$$
$$\underset{(stearin)}{} \longrightarrow 3\,C_{18}H_{35}CO_2Na + C_3H_5(OH)_3$$
$$\underset{(sodium\ stearate)}{} \quad \underset{(glycerin)}{}$$
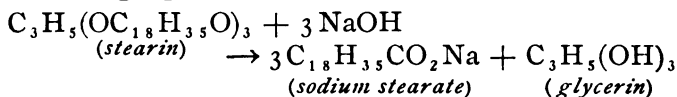
480. Soaps. Soaps consist of the alkalin salts of palmitic, stearic, and oleic acids. Hard soaps contain sodium salts, chiefly of the solid acids, and soft soaps contain potassium salts, principally of oleic acid. The kind of soap also varies with the fats used. Thus, tallow, lard, palm oil, and cocoanut oils make white soap, while the addition of rosin, cotton-seed oil, and house or bone grease, gives the soap a yellow color. Castile soap is made from olive oil.

MANUFACTURE OF SOAP. By means of steam coils the alkalin solution is heated in an immense kettle provided with stirrers, and the fat is added. The mixture is heated to boiling until the saponification is complete. Salt is then added, whereupon the soap separates out at the top. The liquid beneath the soap is drawn off and the glycerin which it contains extracted. The soap is then washed and mixed with any perfume or coloring matter desired, or some "filler," such as sodium silicate, borax, or sand; after it has cooled it is cut into bars, and laid out to dry.

CARBOHYDRATES

The carbohydrates form a numerous group of compounds, the most important members of which are the sugars and starch. They are so named because they contain hydrogen and oxygen in the same proportion as water, and were for that reason formerly considered to be hydrates of carbon. It is now known that such is not the case.

481. Sugars. The name *sugar* may be applied to almost any sweet substance found in fruits, vegetables, or the sap of trees, but it is more commonly used to refer to the sugar which is derived from sugar cane or sugar beets, and which is used on our tables and in cooking. Chemically speaking, however, there are many distinct sugars differing in composition from these two.

482. Cane Sugar, $C_{12}H_{22}O_{11}$. Cane sugar (also called *sucrose* or *saccharose*) is found in a large number of plants, but our supply is obtained from sugar cane or sugar beets. . When a strong sugar solution is allowed to flow over strings hung from a peg, large transparent crystals are formed, which are called *rock candy*. If heated to about 160°, sugar melts, and when cool forms a yellow mass known as *barley sugar*. If heated to about 200°, it is changed into *caramel*, which is used to color liquors and soups.

MANUFACTURE OF CANE SUGAR. Sugar cane is crushed between rollers and the juice boiled with a little lime; the scum is removed from time to time, and the solution is finally filtered. The juice thus clarified is evaporated until the sugar crystallizes from a sample of the solution when it is cooled. The evaporation is then completed in pans placed in a vacuum, as there is danger of discoloring the sugar if it is heated too high, and because, by removing the pressure of the air, boiling takes place at a lower temperature. The mass of crystals is then freed from the adhering liquor by whirling in a centrifugal machine. The solid mass which is left is called *muscovado, raw*, or *brown sugar*, while the thick liquid is *molasses*.

Sugar beets are reduced to a pulp or cut into thin slices, and soaked with water until all the sugar diffuses out of them. The solution is clarified and evaporated, and the sugar separated in much the same

fashion as sugar from cane, but the molasses obtained is not fit for table use.

The refining of sugar obtained from both of the above sources consists in removing the impurities and recrystallizing the sugar. The raw sugar is dissolved in water contained in immense tanks and the solution heated. It is stirred by blowing air into it, and certain substances are added to gather up and deposit the impurities. The solution is then filtered through animal charcoal, which removes all color from it. The resulting colorless sirup is evaporated in vacuum pans to crystallization, and is then run into tanks to crystallize. The crystals are separated out by a centrifugal machine, and the liquid boiled over again or made into table sirups. The crystalline mass is so dried that each grain will be free, and we have the familiar *granulated sugar*.

LACTOSE OR MILK SUGAR. Lactose has the same composition as cane sugar, but its properties are different. It is obtained from milk, and forms white, gritty crystals, which are not so sweet as cane sugar. It is used in making homeopathic pills and infants' foods.

483. Glucose, $C_6H_{12}O_6$. Glucose, *dextrose* or *grape sugar*, is found in many sweet fruits, especially grapes. Raisins (which are dried grapes) are often coated with this sugar. *Levulose, fructose* or *fruit sugar*, is isomeric with glucose, and is often found associated with it, as, for instance, in honey. When cane sugar is boiled with a dilute acid, it takes up water, and both dextrose and levulose are formed:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$
$$(\textit{cane sugar}) \qquad\qquad (\textit{dextrose}) \qquad (\textit{levulose})$$
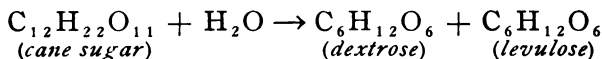
Both these sugars are fermentable, and yield carbon dioxid and alcohol. In alkalin solution glucose is a powerful reducing agent. When sugar is boiled with an alkalin solution of copper sulfate, called

Fehling's solution, red cuprous oxid is formed. This reaction furnishes a test for sugar.

"GLUCOSE." The ordinary commercial mixture called "glucose" is manufactured by boiling starch with dilute sulfuric acid. The liquid products which result are known as "glucose" or "mixing sirup," while the solid product is termed "grape sugar." They all contain some glucose and are a little more than half as sweet as cane sugar. But as they are cheaper than cane sugar, they are used extensively in its place in the manufacture of the poorer grades of jelly, candy, and sirup.

484. Starch. Starch is found in all grains, in most vegetables, and in parts of the majority of plants. It is separated by mechanical processes from the other parts of plants. As usually seen, it forms white lumps or powder, but under the micro-scope it is seen to consist of oval grains, varying somewhat in appearance with the source. Starch is almost insoluble in cold water, but if it be treated with boiling water, the grains swell and burst, and form a solution which is used in laundries as "starch." Immense amounts of starch are used in foods, in laundries, in finishing paper and cloth, and in making glucose.

485. Dextrin. When starch is treated with dilute acids it forms a sticky solution, from which dextrin is prepared. Mucilage contains a large proportion of dextrin.

BREAD. Wheat flour is about three-fourths starch and about one-eighth water and one-eighth gluten; small amounts of inorganic salts and dextrin are also present. In making bread, a little yeast is mixed with flour and water (sometimes also milk) and the resulting dough thoroughly kneaded. When the dough is set in

a warm place to rise, the yeast cells multiply and convert the fermentable sugar present into alcohol and carbon dioxid. This gas, in trying to escape, puffs up the dough, which is thereby made light and porous; the bread "rises." When the bread is baked the high temperature kills the yeast, thus stopping the fermentation. The alcohol, carbon dioxid, and more or less of the water escape and puff up the dough still more. The outside of the bread is exposed to a more direct heat than the interior and becomes harder, thus forming the crust. Most of the starch undergoes no chemical change, but the crust is largely dextrin.

486. Cellulose, $(C_6H_{10}O_5)_n$. Cellulose forms the framework of most vegetable tissues, and is hence very abundant and widely distributed. Wood, cotton, linen, and paper are made up largely of cellulose. When pure, cellulose is a white solid, insoluble in most liquids. Concentrated sulfuric acid will dissolve it slowly, and if the solution is diluted and boiled, the cellulose is converted into a mixture of dextrin and glucose. Cellulose behaves like an alcohol in that it reacts with acids to form esters.

HIGH EXPLOSIVES. Cellulose and also glycerin react with nitric acid to form highly explosive compounds. Nitroglycerin is a yellow, heavy oil, which, when kindled, burns quietly, but if subjected to a sudden shock, as that of an exploding percussion cap, it explodes with great violence.

Dynamite consists of some fine powder, as infusorial earth or wood pulp, soaked with nitroglycerin. *Gun cotton* is cellulose nitrate, and looks very similar to ordinary cotton. It burns rapidly but quietly when ignited, but explodes when a percussion cap is set off in it. *Collodion* is a solution of gun cotton in a mixture of alcohol and ether. When collodion is spread upon a glass plate or the skin, the solvent soon evaporates and leaves a thin film of gun cotton. This film protects

wounds from the action of the air, and it is also utilized in the preparation of " wet process" photographic plates.

Celluloid consists of a mixture of gun cotton and camphor. It is readily molded and is put to a variety of uses. It smells of camphor, is readily set on fire, and burns freely with a smoky flame.

PAPER. Paper is more or less pure cellulose mixed with various other ingredients added for the purpose of imparting a special surface or color. The best paper is made from rags, but that used in newspapers and many books is made from wood.

In making paper, the rags or wood are first reduced to a pulp, which is spread on a wire gauze, dried, and pressed. Wood pulp is commonly made by heating under pressure chips of wood (spruce is best) with a solution of caustic soda, or of sodium (calcium) bisulfite. The pulp is usually mixed with clay, gypsum, aluminum sulfate, or other substances, so as to make it of closer texture and more opaque. The paper is then said to be "filled." The paper on which this book is printed is filled with clay. Paper that is to be used for printing or writing is covered with a "size" consisting of gelatin, rosin, or other substance which will keep the ink from spreading. Most paper is finished by passing it between heavy rollers.

BENZENE DERIVATIVES

487. Coal Tar. In the manufacture of illuminating gas (page 91) there collects in the hydraulic main and condensers a thick, black, bad-smelling liquid, which is called *coal tar.* Some of this is used in preserving timber and in making tarred paper and paint, but most of it is distilled, whereby it is separated into various constituents.

488. Benzene, C_6H_6. Benzene is a light, colorless liquid, not miscible with water; it gives off an odor something like that of illuminating gas. Benzene dissolves fats, resins, iodin, sulfur, and rubber.

Its main use is in the preparation of its derivatives, which are numerous and important.

NOTE. Benzene is sometimes called *benzol*, and should not be confused with ben*zine*, which is one of the products of the distillation of petroleum.

CONSTITUTION OF THE BENZENE MOLECULE. It is believed that the atoms of carbon in the benzene molecule are arranged in a ring, and that every other carbon atom is combined with its neighbor by a double bond. The structural formula is usually written :

$$
\begin{array}{c}
\text{H} \\
| \\
\text{C} \\
\diagup \quad \diagdown \\
\text{H} - \text{C} \qquad \text{C} - \text{H} \\
| \qquad\qquad \| \\
\text{H} - \text{C} \qquad \text{C} - \text{H} \\
\diagdown \qquad \diagup \\
\text{C} \\
| \\
\text{H}
\end{array}
$$
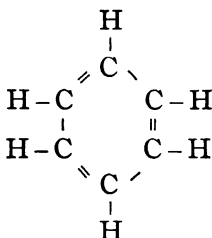
In all of the numerous compounds of benzene this ring-shaped structure remains intact. Not one of the atoms of carbon may be taken away without causing complete decomposition. The derivatives are formed by the substitution of other elements or radicals for the hydrogen.

489. Toluene, C_7H_8. Toluene, which much resembles benzene, may be regarded as methyl benzene, $C_6H_5CH_3$, where one hydrogen atom is replaced by the radical, methyl, CH_3, or as phenyl methane, where one of the hydrogen atoms of methane, CH_4, may be considered to be replaced by the radical, *phenyl*, C_6H_5.

490. Phenol, C_6H_5OH. Phenol is a white, crystalline solid, with a smoky odor and sharp taste. It is corrosive and poisonous. Its solution in water is

called *carbolic acid* and is used as a disinfectant. *Picric acid*, or tri-nitro-phenol, $C_6H_2(NO_2)_3OH$, a derivative of phenol, forms yellow crystals soluble in water. It is used in dyeing silk yellow and in the manufacture of high explosives.

491. Nitrobenzene, $C_6H_5NO_2$. Nitrobenzene is the yellow liquid obtained from the action of nitric acid on benzene. It has the odor of bitter almonds, and, although poisonous, is frequently used in producing the flavor of bitter almonds.

492. Anilin, $C_6H_5NH_2$. Anilin is a colorless oil prepared by the reduction of nitrobenzene. Many compounds known as *anilin dyes* are derived from it.

493. Benzoic Acid, $C_6H_5CO_2H$. Benzoic acid is found in certain gums, and is usually prepared from gum benzoin. It forms small white crystals with a pleasant odor.

494. Benzoic Aldehyde, C_6H_5COH. Benzoic aldehyde, commonly known as *oil of bitter almonds*, is used as a flavoring substance.

495. Salicylic Acid, $C_6H_4OHCO_2H$. Salicylic acid forms white crystals and is used as a food preservative. *Sodium salicylate* is a specific remedy for rheumatism, and *methyl salicylate* is the compound which gives the flavor to wintergreen.

496. Naphthalene, $C_{10}H_8$. Naphthalene also is obtained from coal tar. It forms white crystals which have a disagreeable odor, and are in common use as "moth balls."

497. Glucosides. Glucosides occur in many plants and by the action of ferments are converted into glucose, benzene derivatives, and other compounds. Thus, *amygdalin* is found in laurel leaves,

bitter almonds, and cherry and peach kernels. The ferment *emulsin*, which also occurs in plants, causes the amygdalin to break up into benzoic aldehyde, glucose, and hydrocyanic acid.

The class of compounds known as *tannins* are also glucosides. They occur in the leaves and bark of the oak, hemlock, and pine, as well as in tea, coffee, sumach, gall nuts, and numerous plants. *Gallic* and *tannic* acids are the best known derivatives of the tannins; tannic acid is often called simply tannin. Iron salts produce black compounds with tannin, and its presence may be shown in decoctions of tea, hemlock bark, or oak bark, by the appearance of a black precipitate when ferrous sulfate is added. The best writing ink is made from iron compounds and tannin. When fresh hides are soaked in solutions of tannin, reactions take place which convert the hides into leather; the hides are *tanned*.

498. Alkaloids. Alkaloids are extracted from plants, and are characterized by the physiological effect they have upon animals. They all contain nitrogen, and act like ammonia in having an alkalin reaction and in combining directly with acids to form salts. Many of these salts are used as medicines.

Opium is the dried sap of unripe poppies; it contains several alkaloids, chief of which is *morphine*, used to alleviate pain and induce sleep. *Laudanum* and *paregoric* are preparations of opium. *Quinine* is extracted from the bark of the cinchona tree, and is used as a remedy in fevers. *Cocaine*, obtained from the coca plant, is used largely in dentistry and minor surgery as a local anæsthetic. *Nicotine* occurs in tobacco, and *theine* or *caffeine* in tea and coffee.

APPENDIXES

APPENDIX A

QUALITATIVE ANALYSIS

INTRODUCTORY

Qualitative chemical analysis has to do with the operations and
methods which are employed in finding out what elements and
radicals are contained in a substance or mixture of substances.

Qualitative analysis consists mainly of the study of the solu-
bilities of substances. In the usual scheme of analysis the sub-
stance to be analyzed is first brought into solution. A solution of
a known compound (a reagent) is then added to this solution, and
if a precipitate of certain properties is formed, a definite conclusion
may be drawn as to the presence of certain elements or radicals
in the original substance taken. Other known solutions are added
to the filtrate from this precipitate, and from the formation of
additional precipitates and observation of their properties further
conclusions can be drawn as to the composition of the original
substance

The solubilities of certain salts of the commoner metals permit
of their classification into five groups, which are usually given the
name of the reagent which is added to effect the precipitation.
These groups are:

I. Hydrochloric Acid Group	{ Lead Mercury (*ous* salts) Silver }	Precipitated as chlorids, $PbCl_2$, $HgCl$, $AgCl$, by hydrochloric acid.
II. Hydrogen Sulfid Group	{ Lead Mercury (*ic* salts) Copper Cadmium Bismuth Tin Antimony Arsenic }	Precipitated as sulfids, PbS, HgS, CuS, CdS, Bi_2S_3, SnS or SnS_2, Sb_2S_3, or Sb_2S_5, As_2S_3 or As_2S_5, by hydrogen sulfid. The last three are soluble in yellow ammonium sulfid, the others not.

[i]

III. Ammonium Sulfid Group	{	Aluminum Chromium Iron Cobalt Nickel Manganese Zinc	The first three are precipitated as hydroxids, Al(OH)$_3$, Cr(OH)$_3$, Fe(OH)$_3$, by ammonium hydroxid. The last four are precipitated as sulfids, CoS, NiS, MnS, ZnS, by ammonium sulfid.
IV. Ammonium Carbonate Group	{	Calcium Strontium Barium Magnesium	Precipitated as carbonates, CaCO$_3$, SrCO$_3$, BaCO$_3$, MgCO$_3$ (soluble in NH$_4$Cl), by ammonium carbonate.
V. Alkali Metals	{	Lithium Sodium Potassium Ammonium	Not precipitated by any common reagents.

I. HYDROCHLORIC ACID GROUP

Method of Analysis

Add HCl a little at a time to the solution as long as a precipitate (ptt.) is formed. Shake up well, filter, and wash twice with a little cold water. Punch a hole in the apex of the filter paper and wash the precipitate into a beaker. Boil the water and filter while hot.

Residue: AgCl, HgCl.	Filtrate: PbCl$_2$
Wash with hot water and twice pour over it enough NH$_4$OH to cover it.	Divide into two portions. Portion I. Add K$_2$Cr$_2$O$_7$ or K$_2$CrO$_4$; a yellow ptt. soluble in NaOH indicates the presence of *lead*. Portion II. Add KI; a yellow ptt. soluble in hot water and recrystallizing in plates on cooling proves the presence of *lead*.

Residue:	Filtrate:
Hg·NH$_2$·Cl and Hg. A black residue proves the presence of *mercury*.	AgCl·2NH$_3$ Acidify with HNO$_3$; a white ptt. proves the presence of *silver*.

Reactions of Solutions of Silver, Lead, and Mercurous Salts

SILVER

HCl precipitates AgCl, white, curdy, changing on exposure to the light from lavender to black ; soluble in NH_4OH, forming $AgCl \cdot 2\,NH_3$, from which solution HNO_3 reprecipitates AgCl.

LEAD

HCl precipitates $PbCl_2$, white, flocculent, soluble in hot water, crystallizing in long needles when solution cools.

H_2SO_4 precipitates $PbSO_4$, white.

$K_2Cr_2O_7$ or K_2CrO_4 precipitates $PbCrO_4$, yellow, soluble in NaOH.

KI precipitates PbI_2, yellow, soluble in hot water, from which when cold it crystallizes in shining plates.

H_2S precipitates PbS, black, changed by hot and moderately concentrated HNO_3 into sulfur and $Pb(NO_3)_2$, which is soluble.

MERCURY

HCl precipitates HgCl, white, changed by NH_4OH into a black mixture of $HgNH_2Cl$ and Hg.

II. HYDROGEN SULFID GROUP

Method of Analysis

Warm the filtrate from the Hydrochloric Acid Group and pass a current of hydrogen sulfid through it. Make sure that precipitation is complete by filtering a small portion, diluting the filtrate, and treating it with H_2S a few minutes. Filter and wash thoroughly with hot water. Put a small portion of the precipitate in an evaporating dish ; add a little ammonium polysulfid. If this precipitate dissolves completely, Division A is absent ; if not, treat the remainder of the precipitate with ammonium polysulfid and warm (not *boil*) for about three minutes with occasional stirring. Filter while hot and proceed as indicated in table for Division A.

DIVISION A

Boil the precipitate in an evaporating dish with a small amount of a mixture of equal volumes of strong nitric acid and water until brown fumes cease to be given off freely. Dilute with a little water and filter.

Filtrate: Lead, Bismuth, Copper, Cadmium Salts.			**Residue:** Mercuric Salt.

Filtrate: Lead, Bismuth, Copper, Cadmium Salts.

Add a little strong H_2SO_4 and evaporate with care until *dense* white fumes appear. Add an equal volume of dilute H_2SO_4 and filter.

Residue: Mercuric Salt. Boil with a very little aqua regia. Filter, boil the filtrate until chlorin is expelled, then add $SnCl_2$ and warm. A gray or black ptt. proves the presence of *mercury*.

Filtrate: Bismuth, Copper, Cadmium Salts.	**Residue:** $PbSO_4$

Filtrate: Bismuth, Copper, Cadmium Salts.

Add NH_4OH until strongly alkalin. A deep blue solution proves the presence of *copper*. A white ptt. indicates *bismuth*. Filter and wash.

Residue: $PbSO_4$

Wash, warm the ptt. with ammonium acetate and a few drops of $HC_2H_3O_2$ and filter. To the filtrate add K_2CrO_4 or $K_2Cr_2O_7$. A yellow ptt. soluble in NaOH proves the presence of *lead*.

Filtrate: Copper, Cadmium Salts.

If copper is absent: Make slightly acid with dil. HCl and treat with H_2S. A yellow ptt. proves the presence of *cadmium*.

If copper is present: Acidify with dil. HCl and precipitate with H_2S. Filter and boil the ptt. immediately with dilute H_2SO_4. Filter, rejecting the residue. Dilute the *colorless* filtrate with an equal volume of water and treat with H_2S. A yellow ptt. proves the presence of *cadmium*.

Precipitate: Bi$(OH)_3$ or basic salt of bismuth.

Add two or three drops of HCl to the ptt. in the funnel and allow the filtrate to drop into a beaker of water. A white ptt. proves the presence of *bismuth*.

REACTIONS OF SOLUTIONS OF MERCURIC, CUPRIC, CADMIUM, AND BISMUTH SALTS

MERCURY

H_2S precipitates HgS, black, insoluble in hot and concentrated HNO_3, but changed by prolonged action of that reagent into $Hg(NO_3)_2 \cdot 2\,HgS$, white and insoluble in concentrated HNO_3. Both $Hg(NO_3)_2 \cdot 2\,HgS$ and HgS are changed by aqua regia into sulfur and $HgCl_2$, which is soluble. HgS is insoluble in $(NH_4)_2S$.

$SnCl_2$ reduces $HgCl_2$ to HgCl, white. An excess of $SnCl_2$ reduces the HgCl more or less to mercury, which gives the HgCl a darker color.

COPPER

H_2S precipitates CuS, black, changed by hot and concentrated HNO_3 into sulfur and $Cu(NO_3)_2$, which is soluble. CuS is insoluble in dilute H_2SO_4. CuS is slightly soluble in $(NH_4)_2S$.

NH_4OH precipitates light blue basic salts, readily soluble in excess, producing deep blue solutions of ammonia cupric salts, as $CuSO_2 \cdot 4\,NH_3$.

CADMIUM

H_2S precipitates CdS, varying in color from light yellow to orange according to the conditions under which precipitation takes place; easily soluble in concentrated HCl or in hot and dilute H_2SO_4; changed by hot and concentrated HNO_3 into sulfur and $Cd(NO_3)_2$, which is soluble. CdS is insoluble in $(NH_4)_2S$.

NH_4OH precipitates $Cd(OH)_2$, white, readily soluble in excess, producing ammonia cadmium salts, as $Cd(NO_3)_2 \cdot 4\,NH_3$.

BISMUTH

H_2S precipitates Bi_2S_3, dark brown; changed by hot and concentrated HNO_3 into sulfur and $Bi(NO_3)_3$, which is soluble. Bi_2S_3 is insoluble in $(NH_4)_2S$.

H_4O added in large proportion to solutions of bismuth salts which do not contain too much acid, precipitates basic salts, as $BiOCl$, $(BiO)_2SO_4$, $BiONO_3$, etc.

NH_4OH precipitates $Bi(OH)_3$ or a basic salt, white; insoluble in excess; soluble in dilute HCl.

DIVISION B

Slightly acidify the ammonium sulfid solution with HCl. [If the precipitate is white it is probably only sulfur.] Filter, rejecting the filtrate, as it contains no metals, transfer the precipitate to a beaker, add a little concentrated HCl, heat to boiling for a few minutes, and filter.

Filtrate: Tin, Antimony salts.		Residue: Arsenic Sulfids.
Place a *bright* iron wire or nail in the filtrate, warm gently, let stand for fifteen minutes, and then filter.		Dissolve in hot, conc. HNO_3. Add a little of the solution to a test tube nearly half full of a solution of ammonium molybdate, and warm gently.
Filtrate: $SnCl_2$	**Precipitate:** Antimony (in metallic state).	
Add $HgCl_2$. A white ptt. getting gray when more of $HgCl_2$ is added and heat applied, proves presence of *tin*.	Wash thoroughly and transfer to a beaker. Dissolve in a little conc. HCl to which a few drops of conc. HNO_3 has been added. Evaporate nearly to dryness; then add a large proportion of water. The formation of a white ptt. proves the presence of *antimony*. [Proof may be confirmed by passing H_2S into solution with formation of orange ptt.]	A yellow crystalline ptt. proves the presence of *arsenic*. Also try the special tests.

REACTIONS OF SOLUTIONS OF TIN, ANTIMONY, AND ARSENIC SALTS

TIN (*Stannous*)

H_2S precipitates SnS, dark brown; soluble in warm concentrated HCl; soluble in $(NH_4)_2S$, forming sulfo-stannates, as $(NH_4)_2SnS_3$, from which a dilute acid precipitates SnS_2, yellow.

$HgCl_2$ is reduced by $SnCl_2$ in HCl solution to HgCl, white; an excess of $SnCl_2$ reduces some of the HgCl to mercury, which imparts a darker color to the precipitate.

TIN (*Stannic*)

H_2S precipitates SnS_2, yellow, from solutions not containing too much HCl; soluble in warm concentrated HCl; soluble in $(NH_4)_2S$, forming sulfo-stannates, as $(NH_4)_2SnS_3$.

ANTIMONY (*ous*)

H_2S precipitates Sb_2S_3, orange red; soluble in warm, concentrated HCl; oxidized by hot, concentrated HNO_3, forming sulfur and H_3SbO_4, which is soluble. Sb_2S_3 is soluble in $(NH_4)_2S$, forming sulfo-antimonates, as $(NH_4)_3SbS_4$, from which dilute acids precipitate Sb_2S_5, orange red.

When $SbCl_3$ is added to a large proportion of water, SbOCl, white, is produced, which is changed directly to Sb_2S_3 when treated with H_2S.

ANTIMONY (*ic*)

H_2S precipitates Sb_2S_5, orange red, and resembling Sb_2S_3 in its behavior toward most reagents.

ARSENIC (*ous*)

H_2S precipitates As_2S_3, lemon yellow; almost insoluble in warm, concentrated HCl; oxidized by hot concentrated HNO_3 to H_3AsO_4, which is soluble, sulfur being set free. As_2S_3 is soluble in $(NH_4)_2S$, forming sulfo-arsenates, as $(NH_4)_3AsS_4$, from which HCl precipitates As_2S_5.

ARSENIC (*ic*)

H_2S precipitates As_2S_5, lemon yellow, and resembling As_2S_3 in its behavior toward most reagents. The precipitation takes place slowly and is more complete if the solution is warm, when H_2S reduces the arsenic solution to the arsenious condition and As_2S_3 is precipitated.

$(NH_4)_2MoO_4$, ammonium molybdate, added in excess to a solution of arsenic acid containing HNO_3 precipitates ammonium arseno-molybdate, yellow. Precipitation is best obtained by adding the arsenic solution to a small test tube half full of $(NH_4)_2MoO_4$. The mixture should then be warmed, but should not be heated above 70°, lest MoO_3, white, be precipitated.

III. AMMONIUM SULFID GROUP

METHOD OF ANALYSIS

Add NH_4OH to slight alkalinity, heat to boiling, then add $(NH_4)_2S$ in slight excess; heat again to boiling and allow the precipitate to settle. Filter and wash thoroughly with hot water. Without delay treat the precipitate in an evaporating dish with a mixture of equal volumes of strong HCl and water, stirring well. Filter and wash immediately.

Residue:
Nickel, Cobalt Sulfids.

Test with borax bead; blue, cobalt; brown, nickel.

To detect one of these metals in the presence of the other, dissolve the residue in a little aqua regia. Filter and evaporate to small bulk. Heat to boiling and add an equal bulk of bromin water and then of NaOH. Boil vigorously and add a little bromin water from time to time. Wash thoroughly with boiling water by decantation, filter and boil the ptt. with NH_4OH and NH_4Cl and filter.

Residue:	**Filtrate:**
Cobalt [Co(OH)₃]	Nickel.
$[Co(OH)_3]$	
Test with borax bead.	Treat with H_2S. A black ptt. indicates the presence of *nickel*. Confirm with borax bead.

Filtrate: Iron, Aluminum, Chromium, Zinc, Manganese Chlorids.

Expel any H_2S which may be present by boiling and divide into two unequal portions.

PORTION I. Evaporate the smaller portion to small bulk, add a little chlorin water, and boil until excess of chlorin is expelled. To the cooled solution add KCNS. A red color proves the presence of *iron*.

PORTION II. To the larger portion add a little conc. HNO_3 and boil. Evaporate to small bulk. Nearly neutralize with $(NH_4)_2CO_3$, and, transferring the solution to a flask, add five times its volume of suspended $BaCO_3$. Shake the flask vigorously from time to time for half an hour and then filter.

Precipitate:	**Filtrate:** Zinc,
Chromium, Aluminum, Iron Hydroxids.	Manganese Salts.

Precipitate: Chromium, Aluminum, Iron Hydroxids.

PORTION I. Fuse on platinum foil with Na_2CO_3 and KNO_3. A yellow product indicates the presence of chromium. Dissolve in water and make acid with $HC_2H_3O_2$. A red ptt. with $AgNO_3$ and a yellow ptt. with $Pb(C_2H_3O_2)_2$ proves the presence of *chromium*.

PORTION II. Add an equal bulk of solid Na_2CO_3, half as much $Ba(OH)_2$, and 5 cubic centimeters of water. Boil two or three minutes. Filter, and to the filtrate add NH_4Cl and boil for some time. A white ptt., best seen against a dark background, proves the presence of *aluminum*.

Filtrate: Zinc, Manganese Salts.

PORTION I. Add $HC_2H_3O_2$ and then H_2S. A white ptt. soluble in HCl proves presence of *zinc*.

PORTION II. Put a very little in an evaporating dish, add 1 cubic centimeter of conc. H_2SO_4 and heat until dense white fumes appear. Transfer the cooled contents of the dish to a test tube half full of H_2SO_4, add PbO_2, heat to boiling and allow to stand until suspended matter settles. A red or purple colored solution proves the presence of *manganese*.

REACTIONS OF SOLUTIONS OF NICKEL, COBALT, IRON, MANGANESE, ZINC, ALUMINUM, AND CHROMIUM SALTS

NICKEL

NH_4OH in small proportion precipitates $Ni(OH)_2$, green; if in excess, greenish blue basic salts. The precipitates are soluble in NH_4OH in the presence of ammonium salts. Both solutions and precipitates are changed by $(NH_4)_2S$ into NiS, black.

KOH or NaOH precipitates $Ni(OH)_2$, green; insoluble in excess. $Ni(OH)_2$ is oxidized by boiling with bromin water and NaOH to $Ni(OH)_3$, black; when this is boiled with NH_4OH and NH_4Cl it dissolves.

$(NH_4)_2S$ precipitates from neutral or alkalin solutions NiS, black; somewhat soluble in excess of $(NH_4)_2S$, more readily in the presence of NH_4OH, forming a dark brown solution from which NiS is reprecipitated if the solvent is removed by boiling. NiS is insoluble in cold and not very dilute HCl; it is changed by aqua regia to free sulfur and $NiCl_2$, which dissolves. NiS is oxidized by the oxygen of the air to $NiSO_4$.

A borax bead is colored brown when fused with a compound of nickel.

COBALT

NH_4OH precipitates blue basic salts; easily soluble in NH_4OH in the presence of ammonium salts. Both precipitate and solution are changed by $(NH_4)_2S$ into CoS.

KOH or NaOH precipitates from cold solutions a blue basic salt which, when warmed with the alkali, changes to $Co(OH)_2$, pink. $Co(OH)_2$ is oxidized to $Co(OH)_3$, black, by boiling with bromin water and NaOH. The $Co(OH)_3$ is not affected by boiling with NH_4OH and NH_4Cl.

$(NH_4)_2S$ precipitates from neutral or alkalin solutions CoS, black; insoluble in excess; practically insoluble in not very dilute HCl; attacked by aqua regia, forming sulfur and $CoCl_2$, which dissolves. CoS is oxidized by the air to $CoSO_4$.

A borax bead is colored blue when fused with a compound of cobalt.

IRON (*Ferrous*)

NOTE. As ferrous salts oxidize very readily to ferric, it is only by taking special precautions that a solution of ferrous salt can

be kept from oxidizing. The solution of $FeSO_4$ should be heated with iron filings and H_2SO_4, when the hydrogen will reduce any ferric salt to the ferrous condition.

NH_4OH in neutral solutions precipitates incompletely $Fe(OH)_2$, which oxidizes promptly to compounds first green, then black, and finally reddish brown $Fe(OH)_3$. When these precipitates are treated with H_2S they change into FeS, black.

KOH or NaOH precipitates $Fe(OH)_2$, white, but oxidizing as described above.

$(NH_4)_2S$ precipitates FeS, black; attacked by hot concentrated HNO_3, forming sulfur and $Fe(NO_3)_3$, which dissolves. FeS is soluble in dilute HCl, and on exposure to moist air oxidizes to $FeSO_4$, and finally to a basic ferric sulfate which is brown.

$BaCO_3$, shaken with a cold, neutral, or slightly acid solution of $FeCl_2$, does not precipitate a compound of iron. It is most convenient to employ the $BaCO_3$ suspended in water.

KCNS, potassium sulfocyanate, produces no red coloration in solutions of ferrous salts.

Concentrated HNO_3, or chlorin water, oxidizes ferrous to ferric salts very promptly at the boiling temperature.

IRON (*Ferric*)

NH_4OH, KOH, or NaOH, precipitates $Fe(OH)_3$, reddish brown and gelatinous; changed by $(NH_4)_2S$ into FeS, black.

$BaCO_3$, when shaken with a cold, neutral, or but slightly acid solution of a ferric salt, precipitates $Fe(OH)_3$ or a basic salt.

KCNS, potassium sulfocyanate, in excess, forms with solutions of ferric salts a deep red complex soluble salt.

H_2S reduces acid solutions of ferric salts to the ferrous condition with separation of sulfur.

MANGANESE (*ous*)

NH_4OH, KOH, or NaOH, precipitates $Mn(OH)_2$, white, oxidized quickly to dark brown compounds. The precipitate is changed to MnS by $(NH_4)_2S$.

$(NH_4)_2S$ precipitates MnS, pink, soluble in dilute acids; when exposed to the air it turns brown.

$BaCO_3$, shaken with a cold, neutral, or slightly acid solution of $MnCl_2$, does not precipitate a compound of manganese.

Fusion with Na_2CO_3 and KNO_3 oxidizes manganese compounds to green salts of manganic acid, K_2MnO_4 and Na_2MnO_4.

PbO$_2$, lead dioxid, boiled with H$_2$SO$_4$ and a little of a manganese compound, oxidizes the latter to permanganic acid, HMnO$_4$, which imparts a pink or purple color to the solution. If a chlorid or HCl be present in any considerable quantity it must be removed by evaporating with concentrated H$_2$SO$_4$ until dense fumes appear.

ZINC

NH$_4$OH produces in neutral solutions a partial precipitation of Zn(OH)$_2$, white and gelatinous; soluble in ammonium salts producing double salts; changed by (NH$_4$)$_2$S into ZnS.

H$_2$S precipitates ZnS, white, incompletely from neutral solutions of zinc salts of the inorganic acids; it is soluble in most dilute acids, but is only slightly soluble in acetic acid, and wholly insoluble in a solution containing an alkalin acetate, as NaC$_2$H$_3$O$_2$.

(NH$_4$)$_2$S precipitates ZnS, white.

BaCO$_3$, when shaken with a cold, neutral, or but slightly acid solution of ZnCl$_2$, does not precipitate any compound of zinc.

ALUMINUM

NH$_4$OH precipitates Al(OH)$_3$, white, gelatinous; somewhat soluble in excess, the Al(OH)$_3$ being reprecipitated by heat.

(NH$_4$)$_2$S precipitates Al(OH)$_3$, as the sulfid is decomposed by water.

BaCO$_3$, when shaken with a cold, neutral, or slightly acid solution of AlCl$_3$, precipitates Al(OH)$_3$ or basic carbonates.

CHROMIUM

NH$_4$OH precipitates Cr(OH)$_3$, green, gelatinous, difficultly soluble in excess and reprecipitated by boiling.

(NH$_4$)$_2$S precipitates Cr(OH)$_3$.

BaCO$_3$, when shaken with a cold, neutral, or but slightly acid solution of CrCl$_3$, precipitates Cr(OH)$_3$ or basic carbonates.

Fusion with KNO$_3$ and Na$_2$CO$_3$ oxidizes chromium compounds to K$_2$CrO$_4$ and Na$_2$CrO$_4$, yellow. If the fused mass is dissolved in water and the solution acidified with acetic acid, the addition of lead acetate precipitates PbCrO$_4$, yellow.

IV. AMMONIUM CARBONATE GROUP

(*The Alkalin Earth Metals*)

METHOD OF ANALYSIS

To the solution add NH_4Cl, NH_4OH, and then $(NH_4)_2CO_3$. Warm, and if a precipitate appears, filter and wash.

Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$		Filtrate: Mg. salt.
Pour small portions of warm acetic acid upon the ptt., avoiding an excess, until it is dissolved. To a small portion of the solution add $K_2Cr_2O_7$, and if a ptt. appears add $K_2Cr_2O_7$ to all of the solution, and warm and filter.		Add NH_4OH and Na_2HPO_4. Rub the inner surface of the test tube with a glass rod. A crystalline ptt. proves the presence of *magnesium*.
Precipitate: $BaCrO_4$	**Filtrate:** $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$	
Dissolve in HCl, warm the solution and add a few drops of H_2SO_4. A white ptt. (which, however, may appear yellow from the $K_2Cr_2O_7$ in the solution) proves the presence of *barium*.	Make alkalin with NH_4OH, add $(NH_4)_2CO_3$ and warm. Filter the ptt. (if none appears, Sr and Ca are absent), wash thoroughly, and dissolve on the filter with the least possible quantity of HCl. Evaporate *just to dryness*, dissolve in a little water, filter if not clear, and evaporate to small bulk. Divide into two portions.	

PORTION I $SrCl_2$	PORTION II $CaCl_2$
Add a little $CaSO_4$, heat to boiling, and if no ptt. appears at once let stand for at least ten minutes. A fine white ptt. proves the presence of *strontium*.	Add a little K_2SO_4 and heat to boiling. If a ptt. forms, filter it off and to the filtrate add NH_4OH till alkalin, then $(NH_4)_2C_2O_4$ and warm. A white ptt. proves the presence of *calcium*.

REACTIONS OF SOLUTIONS OF BARIUM, STRONTIUM, CALCIUM, AND MAGNESIUM SALTS

BARIUM

Na_2CO_3 or (NH_4) CO_3 precipitates from neutral or alkalin solutions $BaCO_3$, white, flocculent at first, but becoming crystalline when gently warmed. $BaCO_3$ is very slightly soluble in NH_4Cl; freely soluble in HCl and acetic acid, $HC_2H_3O_2$, with effervescence.

H_2SO_5 precipitates $BaSO_4$, white, practically insoluble in water, acids, or alkalis.

Na_2CO_3 or $(NH_4)_2CO_3$ precipitates $SrCO_3$, resembling $BaCO_3$.

STRONTIUM

H_2SO_4 precipitates $SrSO_4$. Calcium sulfate, although but slightly soluble in water, is more soluble than $SrSO_4$, so that $CaSO_4$ will precipitate $SrSO_4$ from a concentrated solution of a strontium salt. Precipitation is more complete when the mixture is warmed or when a concentrated solution of K_2SO_4 is used instead of the $CaSO_4$.

K_2CrO_4 or $K_2Cr_2O_7$ does not precipitate $SrCrO_4$ from dilute solutions acidified with $HC_2H_3O_2$.

CALCIUM

Na_2CO_3 or $(NH_4)_2CO_3$ precipitates $CaCO_3$, resembling $BaCO_3$.

K_2CrO_4 or $K_2Cr_2O_7$ produces no precipitate in dilute solutions acidified with $HC_2H_3O_2$, since $CaCrO_4$ is soluble in both water and $HC_2H_3O_2$.

$(NH_4)_2C_2O_4$ precipitates CaC_2O_4, white, crystalline.

H_2SO_4 or a soluble sulfate, as K_2SO_4, precipitates $CaSO_4$ only from concentrated solutions, and then but partially.

MAGNESIUM

NH_4OH precipitates from neutral solutions containing no ammonium salts one-half of the magnesium as $Mg(OH)_2$. The other half unites with the ammonium salt which is formed to produce double salts, such as $MgCl_2 \cdot 2NH_4Cl$. These double salts are soluble in water and not precipitated by NH_4OH or $(NH_4)_2CO_3$. The object of adding NH_4Cl in the analysis is to form the double salt and thus prevent the precipitation of the magnesium.

Na_2HPO_4 or $NaNH_4HPO_4$ precipitates from solutions of double salts, such as $MgCl_2 \cdot 2 NH_4Cl$, in the presence of NH_4OH, $MgNH_4PO_4$, white and crystalline. Crystallization may be hastened by stirring the solution with a glass rod.

V. THE ALKALI METALS: AMMONIUM, SODIUM, POTASSIUM

METHOD OF ANALYSIS

Ammonia. Put a little of the original substance in a small beaker and add NaOH. Cover the beaker with a watch glass, on the under side of which is placed a moistened piece of red litmus paper. Heat gently, but not to boiling. If the litmus paper turns blue the presence of *ammonia* is proved.

Sodium and Potassium. Evaporate the filtrate from the ammonium carbonate group to dryness and heat until no more fumes of ammonium salts are given off. Divide the residue into two portions.

PORTION I. Sodium, Potassium Salts.	PORTION II. Potassium, Sodium Salts.	
Moisten a small portion with HCl, slip a clean platinum wire into it and introduce into the Bunsen flame. A yellow flame proves the presence of *sodium;* a violet flame proves the presence of *potassium*. If sodium is present, view the flame through a blue glass, whereby the yellow rays are cut off, but the violet allowed to pass.	Dissolve in least possible amount of water and divide solution into two portions.	
	PORTION I.	PORTION II.
	Add platinum chlorid solution and keep under observation for some time. A yellow ptt. proves presence of *potassium*.	Add picric acid solution. A yellow ptt. indicates presence of *potassium*.

REACTIONS OF SOLUTIONS OF AMMONIUM, POTASSIUM, AND SODIUM SALTS

AMMONIA

KOH or NaOH when warmed with an ammonium salt liberates ammonia, which turns moist red litmus paper blue.

When any ammonium salts are heated they break up into

volatile constituents so that through heat ammonia may be separated from non-volatile substances.

SODIUM

Flame test. A sodium salt introduced into a Bunsen flame on a platinum wire colors it an intense yellow.

POTASSIUM

Platinum chlorid, $PtCl_4$, produces a yellow precipitate.

Picric acid produces a yellow precipitate.

Flame test. A potassium salt introduced into a Bunsen flame on a platinum wire colors it violet. As this color is marked by even a very small proportion of sodium, if that element is present, the flame should be observed through blue glass, which absorbs the yellow light.

DETECTION OF ACIDS

I. BARIUM CHLORID GROUP

Sulfuric acid, H_2SO_4, precipitates $BaSO_4$, white, insoluble in HCl.

In neutral solution phosphoric acid, H_3PO_4, precipitates Ba_3PO_4, white, soluble in HCl.

Sulfurous acid, H_2SO_3, precipitates $BaSO_3$, white, soluble in HCl with evolution of SO_2 (odor).

II. SILVER NITRATE GROUP

Hydrochloric acid, HCl, precipitates AgCl; white curds very soluble in NH_4OH.

Hydrobromic acid, HBr, precipitates AgBr, pale yellow, slowly soluble in NH_4OH.

Hydriodic acid, HI, precipitates AgI, yellow, very slightly soluble in NH_4OH.

III. SPECIAL TESTS FOR SOME COMMON ACIDS

Carbonates. Most carbonates give up their carbon dioxid when acted upon by HCl or HNO_3. (See Experiment 67.)

Sulfids. HCl evolves H_2S readily from the sulfids of the alkali and alkalin earth metals, and from sulfids of magnesium, manganese, zinc, and iron; less readily from those of lead, bismuth, cadmium, antimony, tin, nickel, and cobalt; from other sulfids with difficulty or not at all.

H_2S blackens filter paper moistened with lead acetate solution.

A sulfid, when fused with a small piece of solid NaOH on a crucible cover, forms Na_2S, which, when moistened and placed on a silver coin, gives a black stain of Ag_2S.

Acetates. Concentrated H_2SO_4 when warmed with an acetate liberates acetic acid, $HC_2H_3O_2$, recognizable odor. (See also ethyl acetate, Experiment 221.)

In neutral solution FeCl gives a dark red color to a solution of an acetate.

Nitrates. (See Experiment 129.)

THE METRIC SYSTEM OF WEIGHTS AND MEASURES

The metric system of weights and measures is employed in the affairs of everyday life in most of the countries of continental Europe, and is almost exclusively used in science.

The fundamental unit is the *meter*, which is a unit of length a little over a yard long. The other units of length are derived from the meter by successively multiplying and dividing it by ten. The names of these derived units are indicated by prefixes. Thus, the multiple prefixes are the Greek words for ten, *deca–*, hundred, *hecto–*, and thousand, *kilo–*, and the sub-multiple prefixes are the Latin words for ten, *deci–*, hundred, *centi–*, and thousand, *milli–*.

The unit of weight or mass is the *gram*, which is the weight of a cubic centimeter of water at 4°. The same prefixes as are given above are used in expressing the names for the multiples and sub-multiples of the gram.

The unit of volume is the *liter*, which is the volume occupied by 1,000 cubic centimeters (one cubic decimeter of water); 1,000 grams (one kilogram) of water occupies one liter at 4°.

In this system fractions must always be expressed decimally, and only one unit should be employed in designating a quantity measured. Thus, the fractions ½, ⅓, ¾, etc., are written 0.5, 0.33, 0.75, and so on. Also the weight of an object is not given as nine grams, four decigrams, and six centigrams, even when abbreviated into $9^{g.}$, $4^{dg.}$, and $6^{cg.}$, but should be written $9.46^{g.}$

The relations between the units, multiples, and sub-multiples of the metric system are shown in the

TABLE OF THE METRIC SYSTEM

Length	*Weight*	*Volume*	*Notation*
Kilometer_____	Kilogram _____	Kiloliter _____	1000.
Hectometer _____	Hectogram ____	Hectoliter_____	100.
Decameter_____	Decagram _____	Decaliter _____	10.
METER_____	GRAM _____	LITER_____	1.
Decimeter _____	Decigram _____	Deciliter _____	0.1
Centimeter _____	Centigram _____	Centiliter _____	0.01
Millimeter _____	Milligram _____	Milliliter _____	0.001

It is evident from the table that 10 millimeters equal one centimeter, 10 centimeters equal one decimeter, 10 decimeters equal one meter, 10 meters equal one hectometer, and 10 hectometers equal one kilometer. Analogous statements are true for the units of weight and volume.

The abbreviations most often used in this book are: *cm.* for centimeter; *c.c.* for cubic centimeter; *l.* for liter; and *g.* for gram.

The relations of the weights and measures of the metric system to the weights and measures commonly used in English-speaking countries are shown by the

TABLE OF METRIC EQUIVALENTS

One meter _____	=	39.37	inches
One kilometer _____	=	0.62	mile
One centimeter _____	=	0.39	inch
One liter _____	=	1.06	liquid quart
One gram _____	=	15.43	grains
One kilogram _____	=	2.2	pounds (Avoir.)
One metric ton _____	= 2204		pounds
One inch _____	=	2.54	centimeters
One mile _____	=	1.61	kilometers
One cubic inch_____	=	16.39	cubic centimeters
One liquid quart _____	=	0.95	liter
One pound (Avoir.)_____	=	0.45	kilogram
One ounce _____	=	28.35	grams
One grain (Apoth)_____	=	0.0648	gram

APPENDIX C

INSTRUMENTS FOR WEIGHING AND MEASURING

The Thermometer. The thermometer is an instrument for measuring temperatures. Its action depends upon the fact that liquids expand when heated, and contract when cooled. The liquids in common use are mercury or alcohol ; water is not suitable, as it freezes at too high a temperature. Chemical thermometers (Fig. *a*) consist of a glass tube with minute bore, which is blown out into a bulb at the end. The bulb is almost invariably made cylindrical in shape so that the thermometer may be thrust through a cork closing a flask, test tube, or bottle, the temperature of the interior of which is to be found. Details as to the making of thermometers cannot be gone into here, but brief mention may be made of the method employed in graduating the instrument.

The bulb is placed in a dish filled with melting ice, and the position of the liquid in the stem marked on the glass. The instrument is then placed in steam issuing from water which is kept briskly boiling under a pressure of one atmosphere. The liquid expands much more than does the glass and rises in the stem. This new position is also
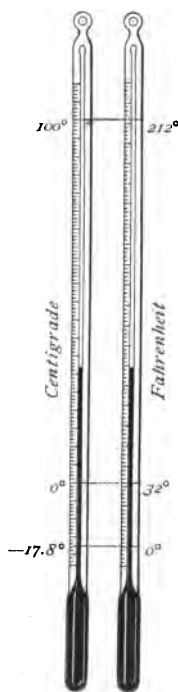
Fig. *a* —
THERMOMETERS

marked on the glass. The portion of the stem between the points thus fixed is divided into a certain number of equal parts, the number depending upon what scale is adopted. The stem above and below these fixed points is likewise divided into parts which are equal to those between the two fixed points.
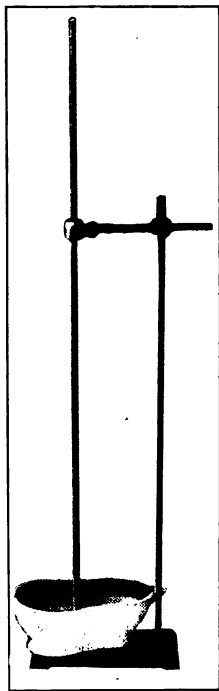
Fig. *b* — A SIMPLE BAROMETER

In the *Centigrade scale*, which is in general use in continental Europe, and in almost exclusive use among scientists, the interval between the temperature of melting ice and boiling water is divided into 100 equal parts; the lower temperature is set at 0° and the higher at 100°. The Centigrade scale alone is employed in this book.

In the *Fahrenheit scale*, which is in general use in English-speaking countries, the interval between the fixed points is divided into 180 equal parts, and the temperature of melting ice is set at 32° and that of boiling water at 212°.

The value of a Centigrade degree is 1.8 times that of a Fahrenheit degree, and 32° Fahrenheit marks the same temperature as 0° Centigrade.

To convert degrees C. into degrees F., multiply by 1.8 and add 32. To convert degrees F. into degrees C., subtract 32 and divide by 1.8.

The Barometer. The barometer is used for measuring the pressure of the atmosphere. In its simplest form it consists of a straight glass tube, about a meter long and closed at one end. This is completely filled

with mercury, which is boiled in the tube in order to drive out every trace of air or moisture, and its open end then placed under the surface of mercury in a dish (Fig. *b*). The mercury falls in the tube to a height of about 76$^{cm.}$. The liquid does not all run out of the tube because the atmosphere pressing down upon the mercury in the dish pushes it up until the weight of liquid in the tube exactly balances the pressure of the atmosphere. If for any cause the pressure of the atmosphere

Fig. *c* — A TRIP BALANCE

becomes greater, it will push the mercury higher up in the tube ; and in a similar fashion, if the atmospheric pressure becomes less, it cannot support so long a column, and accordingly the liquid in the tube falls somewhat.

The Balance. The balance serves to find the weight of an object. When the weight is to be ascertained only to tenths of grams, the form of balance known as the "trip" (Fig. *c*) is excellent. The weights accompanying need have no pieces less than 5$^{g.}$, as the beam and sliding weight in the front permit of the weighing to tenths of grams up to 5$^{g.}$.

In the quantitative work of this book, a balance weighing to hundredths of grams at least is required.
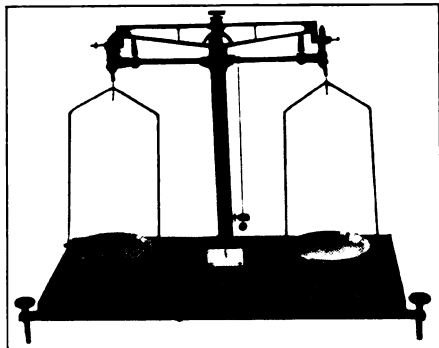
Fig. *d* — AN EQUAL-ARMED BALANCE

Balances sensitive to a milligram are even better, but are much more expensive and must be enclosed in a glass case to prevent currents of air from making them work too erratically. Either an equal-armed balance (Fig. *d*) or an unequal-armed one (Fig. *e*) may be used. Of the former there are numerous excellent makes on the market. They require the use of a box of weights containing tenths and hundredths of grams.

The form of balance in Fig. *e* was devised by the author for the quantitative work of the elementary chemistry laboratory. Its advantages are ease in moving about, rapidity of weighing, and "non-losableness" of the weights, which are rings moving along the beam.
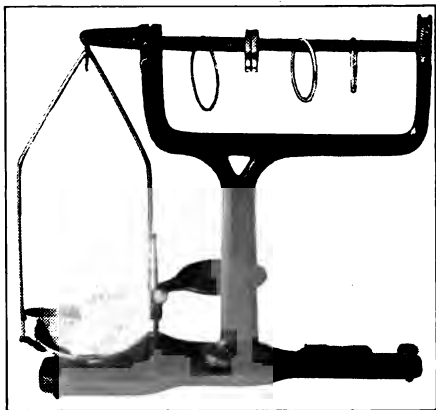
Fig. *e*—UNEQUAL-ARMED BALANCE

RULES TO BE OBSERVED IN WEIGHING

1. *Always leave the balance and weight in a clean and usable condition.*

2. *Never handle the weights with the fingers; use forceps.*

3. *Do not weigh anything but metals* (mercury and sodium excepted) *on the bare scale pan.* Liquids should be weighed in a dish or a beaker, the weight of which has already been found. Solids should be placed on a piece of paper creased twice at right angles so as to sink in a little at the center (Fig. *c*).

Graduated Vessels. For measuring rather large volumes of liquids *graduated cylinders* (Figs. *f* and *g*) of 250 *c.c.* or 50 *c.c.* capacity are used. *Volumetric flasks* (Fig. *h*) are also employed. For measuring small volumes of liquids *pipettes* (Fig. *i*) and *burettes* (Fig. 54, page 77) are used. Pipettes are usually graduated to deliver 5 *c.c.*, 10 *c.c.*, 25 *c.c.*, or 50 *c.c.*. In using a pipette, its tip is dipped into the liquid, which is then sucked up nearly to the top by the mouth, and the upper opening quickly closed with the finger. By lifting up the fore finger so as to let air into the upper part of the pipette the liquid may be

Fig. *f* — 250 *c.c.*
CYLINDER

Fig. *g* —
50 *c.c.*
CYLINDER
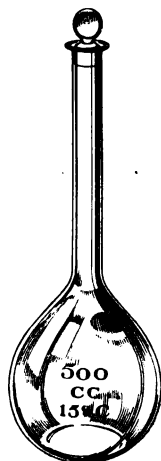
Fig. *h* — VOLU-
METRIC FLASK

made to drop out until its level comes even with the mark on the stem.   The definite volume of liquid thus measured may then be delivered into the vessel in which it is to be used.

Burettes are usually graduated into tenths of cubic centimeters and may hold either 25 *c.c.* or 50 *c.c.*; but as sometimes the spaces are divided into 0.2 *c.c.*, that is, fifths of a cubic centimeter, a burette should be carefully examined before it is used in order that it may be read correctly according to its scale of division.   They are clamped vertically to a support and filled by pouring in the liquid.   Enough liquid is allowed to run out by opening the clamp to drive out all air in the delivery tube, and then by noting the reading of the level of the liquid in the burette, the required volume may be run out into the vessel being used.

A convenient stopcock consists of a glass bead made from a rod a little larger in diameter than the bore of the bit of rubber tubing attached to the burette.   This bead is slipped into the rubber tube between the burette and the delivery tip.   By squeezing the rubber a little, a channel is formed between it and the bead, through which the liquid in the burette may flow. The size of this channel can be regulated with such ease that the liquid may be delivered with great nicety.

Fig. *i*
PIPETTE
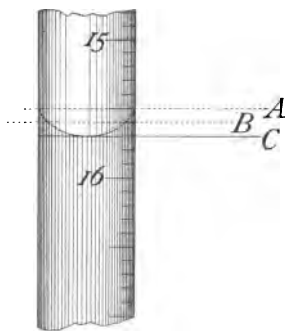
Fig. *j* — READING A BURETTE
The correct reading is along C.
Readings such as A and B must
not be taken

The surface of liquids which *wet* glass is curved upward near

the glass so that in small tubes the surface is concave.
The name of *meniscus* has been given to this curved
surface. The position of a liquid surface with respect
to a scale is always reckoned at the lowest point in the
meniscus, and the eye should be placed so that a line
passing from it to the tube is perpendicular to the tube
(Fig. *j*). In the case of liquids which, like mercury, do
not wet glass, the meniscus is convex, and readings are
taken at its highest point.

It is a good plan for the student to determine the
capacity of his test tubes, beakers, and flasks by pouring
water into them from one of the above vessels. Their
volume once determined, no time is lost in ascertaining
what size of beaker, flask, or test tube is to be used in
the experiments ; they may also serve as rough and
ready measuring vessels.

TABLE I — PHYSICAL CONSTANTS OF

NAME OF ELEMENT	Name of Discoverer and Date of Discovery	Symbol	Formula
Aluminum	Wöhler (1827)	Al	Al
Antimony	Basil Valentine (1460)	Sb	Sb
Argon	Ramsay and Rayleigh (1894)	A	A
Arsenic	Albert Magnus (13th cent.)	As	As₄
Barium	Davy (1808)	Ba	Ba
Bismuth	Basil Valentine (15th cent.)	Bi	Bi
Boron	Gay-Lussac and Thenard (1808)	B	B
Bromin	Balard (1826)	Br	Br₂
Cadmium	Stromeyer (1841)	Cd	Cd
Calcium	Davy (1808)	Ca	Ca
Carbon	Known from earliest times	C	C
Chlorin	Scheele (1774)	Cl	Cl₂
Chromium	Vauquelin (1797)	Cr	Cr
Cobalt	Brand (1735)	Co	Co
Copper	Known from earliest times	Cu	Cu
Fluorin	Moissan (1886)	F	F₂
Gold	Known from earliest times	Au	Au
Hydrogen	Cavendish (1776)	H	H₂
Iodin	Courtois (1812)	I	I₂
Iron	Known from earliest times	Fe	Fe
Lead	Known from earliest times	Pb	Pb
Lithium		Li	Li
Magnesium	Liebig and Bussy (1830)	Mg	Mg
Manganese	Gahn and John (1807)	Mn	Mn
Mercury	Known from earliest times	Hg	Hg
Nickel	Cronstedt (1751)	Ni	Ni
Nitrogen	Rutherford (1772)	N	N₂
Oxygen	Priestley (1774)	O	O₂
Phosphorus	Brand (1674)	P	P₄
Platinum	Waston (1750)	Pt	Pt
Potassium	Davy (1807)	K	K
Silicon	Berzelius (1823)	Si	Si
Silver	Known from earliest times	Ag	Ag
Sodium	Davy (1807)	Na	Na
Strontium	Davy (1808)	Sr	Sr
Sulfur	Known from earliest times	S	S₈
Tin	Known from earliest times	Sn	Sn
Zinc	15th century	Zu	Zn

TABLES

Some of the Elements

Atomic Weights			Valence	Melting Point	Boiling Point	Specific Gravity [1]
H = 1	O = 16	Approximate				
26.9	27.1	27	III	700 (?)	?	2.67
119.3	120.2	120	III, V	440	1300 (?)	6.72
39.6	39.9	40	....	....	....	....
74.4	75.0	75	III, V	446–457	Red heat	5.69
136.4	137.4	137	II	Above that of cast iron	?	3.75
206.9	208.5	208	III, V	268	1700	9.9
10.9	11.	11	III	In electric furnace	?	2.6
79.36	79.96	80	I	−7.3	63	3.1 (liq.)
111.6	112.4	112	II	320	770	8.72
39.8	40.1	40	II	Red heat	?	1.6–1.8
11.91	12.00	12	IV	?	?	Diamond 3.5 Graphite 2.2 Charcoal 1.5
35.18	35.45	35.5	I	−102	−34	1.33 (liq.)
51.7	52.1	52	II, III	?	?	6.7
58.56	59.0	59	II	1800	?	8.6
63.1	63.6	63.5	I, II	1050	?	8.9
18.9	19.	19	I	....	....	?
195.7	197.2	197	III	1030	?	19.3
1.000	1.008	1	I	....	−252.5	1
125.90	126.85	127	I	114	120	4.95
55.5	55.9	56	II, III	1100	?	7.88
205.35	206.9	207	II, IV	325	?	11.37
6.98	7.03	7	I	180	?	0.59
24.18	24.36	24	II	750	1100	1.75
54.6	55.0	55	II	....	....	7.2
198.5	200.0	200	I, II	−38.9	357	13.59
58.3	58.7	58.5	II	1600	?	8.9
13.93	14.04	14	III, V	−203	−194	13.93
15.88	16.00	16	II	....	−1825	15.88
30.77	31.0	31	III, V	44.2	287	Yellow 1.83 Red 2.21
193.3	194.8	195	IV	2000	?	21.5
38.86	39.15	39	I	62.1	667	4.9
28.2	28.4	28	IV	Above cast iron	?	2.5
107.12	107.93	108	I	1000	?	10.5
22.88	23.05	23	I	97.6	742	0.97
86.94	87.6	87	II	Red heat	?	2.5
31.83	32.06	32	II, IV, VI	114.5	448	2.0
118.1	119.0	119	II, IV	227	1600	7.3
64.9	65.4	65	II	420	930	7.1

[1] Referred to water if the element be in a solid or a liquid state; to hydrogen if in a gaseous state.

TABLE II—TENSION OF WATER VAPOR

15°	12.7 mm.	23°	20.9 mm.
16°	13.5 mm.	24°	22.2 mm.
17°	14.4 mm.	25°	23.6 mm.
18°	15.4 mm.	26°	25.0 mm.
19°	16.3 mm.	27°	26.5 mm.
20°	17.4 mm.	28°	28.1 mm.
21°	18.5 mm.	29°	29.8 mm.
22°	19.7 mm.	30°	31.5 mm.

TABLE III — SOLUTIONS TO BE PREPARED

The figures in parentheses indicate the number of cubic centimeters (if the substance is a liquid) and the number of grams (if the substance is a solid) that are to be dissolved in water; the solution should then be diluted to one liter.

Acetic acid, (140) of 80% acid.

Alum (any one), (100).

Aluminum chlorid, (100).

Aluminum sulfate, (25).

Ammonium carbonate. Dissolve 200 g. in a mixture of 100 c.c. of conc. NH_4OH and 600 c.c. of water, and after solution is complete dilute to one liter.

Ammonium chlorid, (100).

Ammonium hydroxid, (250) of conc. NH_4OH.

Ammonium molybdate. Dissolve 50 g. of molybdic acid in a mixture of 100 c.c. of conc. NH_4OH and 150 c.c. of water. Dilute 250 c.c. of conc. nitric acid with 500 c.c. of water and pour into first solution slowly and with constant stirring. Let stand in a warm place for 48 hours and decant the clear supernatant solution for use.

Ammonium nitrate, (25).

Ammonium oxalate, (50).

Ammonium polysulfid. Dissolve some sulfur in ammonium sulfid solution.

Ammonium sulfid. Pass H_2S into one liter of conc. NH_4OH to saturation. Then add 750 c.c. conc. NH_4OH and one liter of water.

Ammonium sulfocyanid (also called thiocyanate), (10).

Antimony chlorid. Dissolve 25 g. in a mixture of 250 c.c. of conc. HCl and 750 c.c. of water.

Arsenic chlorid. Dissolve 50 g. sodium arsenite, Na_3AsO_3, in 1,000 c.c. of water and add in small portions conc. HCl until further addition occasions no effervescence.

Barium carbonate. In suspension in water.

Barium chlorid, (60).

Barium hydroxid. Dissolve 50g. in one liter of hot water, let stand over night, and filter or decant. Keep in tightly stoppered bottle.

Bismuth nitrate, (25). The solution must contain a little free nitric acid.

Boric acid, (40). Saturated solution.

Bromin solution. Dissolve 25g. of KBr in 250$c.c.$ of water, add 6g. (2 $c.c.$) of bromin, and shake until bromin is dissolved.

Bromin water. Put 40g. (13 $c.c.$) in a liter of water. Keep bottle tightly stoppered and in the dark.

Cadmium chlorid, (25).

Calcium chlorid, (25).

Calcium hydroxid, (lime water). Put some freshly slaked lime in a bottle, fill bottle with water, shake, and when solution is clear, decant and reject it, as it may contain some impurities from the lime. Fill the bottle with water again and shake well.

Calcium sulfate. Prepare saturated solution in same manner as lime water above.

Chromium chlorid, (25). To 1,000.$c.c.$ of potassium dichromate solution add 50$c.c.$ of conc. HCl and 25 $c.c.$ of alcohol. Boil for half an hour gently and, if, after standing over night, the solution is not clear green add more alcohol and boil again.

Chromium sulfate, (30).

Chlorin water. Pass chlorin gas into water until it smells strongly of the gas. Better make small quantities when needed by adding a little conc. HCl to a few crystals of $KClO_3$ in a test tube and as soon as the gas escapes from mouth of tube, adding water to stop reaction.

Cobalt chlorid, (50).

Cobalt nitrate, (35).

Cochineal. Grind a little with water and dilute to desired tint.

Copper nitrate, (40).

Copper sulfate, (35).

Disodium hydrogen phosphate, (120).

Ferric chlorid, (100).

Ferrous sulfate. Dissolve 150g. of clear crystals in one liter of water, and add 5 $c.c.$ of conc. H_2SO_4 and a few pieces of iron (tacks or small nails).

Hydrochloric acid, (250) of conc. acid.

Indigo. Slowly add 10g. of powdered indigo to 25 $c.c.$ of fuming sulfuric acid. Let stand for a day and then add slowly with constant stirring to one liter of water.

Lead acetate, (90).

Lead nitrate, (40).

Litmus. Grind a little with water to a paste and dilute to desired tint.

Magnesium chlorid, (25).

Magnesium sulfate, (100).

Manganous chlorid, (75).

Manganous sulfate, (35).

Mercuric chlorid, (30).

Nessler's Reagent. Dissolve 35 *g.* of potassium iodid in 100 *c.c.* of water ; also dissolve 16 *g.* of mercuric chlorid in 300 *c.c.* of water. Add the latter solution to the former slowly with constant stirring until the precipitate ceases to be redissolved. Then add a solution of 65 *g.* of potassium hydroxid in 60 *c.c.* of water and filter. Put the solution into a number of small bottles and cover the corks with paraffin. Keep in a cool, dark place, and when the solution is needed, do not open more than one bottle at a time.

Nickel chlorid, (25).

Nickel nitrate, (35).

Nitric acid, (250) of conc. acid.

Phenolphthalein. Dissolve one gram in 100 *c.c.* of alcohol and dilute with water until a precipitate begins to form ; then add enough alcohol to clarify solution.

Platinum chlorid. Use commercial solution, or, dissolve scrap platinum in aqua regia, evaporate nearly to dryness, and dissolve residue in enough water to make about 10 per cent solution.

Potassium bromid, (30).

Potassium chromate, (100).

Potassium chlorid, (50).

Potassium dichromate, (50).

Potassium ferricyanid, (30).

Potassium ferrocyanid, (50).

Potassium hydroxid, (150).

Potassium iodid, (25).

Potassium nitrate, (100).

Potassium sulfate, (100).

Potassium sulfocyanate, (50).

Silver nitrate, (40). Keep in amber glass bottle.

Sodium acetate, (130).

Sodium ammonium phosphate, (70).

Sodium chlorid, (100).

Sodium hydroxid, (175).

Sodium sulfite, (200).

Stannous chlorid. Dissolve 50 *g.* in 100 *c.c.* of hot conc. HCl and keep a few pieces of tin in the solution. Make only when needed, as it does not keep well.

Starch paste. Grind about 10 *g.* to a paste with a little cold water, then boil with 250 *c.c.* of water until clear.

Strontium chlorid, (30).

Strontium nitrate, (30).

Sulfuric acid, (250) of conc. acid. Pour acid in small portions, with stirring, into the full amount of water required for dilution.

Tartar emetic, (100).

Zinc chlorid, (50).

Zinc sulfate, (140).

SIGNIFICANT FIGURES AND FORMS OF RECORD IN QUANTITATIVE WORK

All the figures of a number are called *significant* excepting the ciphers at the right of a whole number and the ciphers at the left of a decimal fraction ; thus, the significant figures of 30,600 as well as of 0.000306 are 306.

In all measurements one significant figure more than is known to be correct is kept in the number expressing the result of the measurement ; this figure is said to be the *least accurate figure* or the *doubtful figure* of the number. Thus, suppose the volumes of water displaced from an aspirating bottle in three determinations of the weight of a liter of oxygen (Experiment 16) were found to be in each case, 1685 $^{c.c.}$, 1680 $^{c.c.}$, and 1689 $^{c.c.}$; the sum of these three numbers is 5054, and their mean is 1684.666 $+$ $^{c.c.}$, or 1684.66$\frac{2}{3}$ $^{c.c.}$, or 1684.67 $^{c.c.}$. No one of these is proper, for each assumes a greater accuracy than we have any warrant for ; moreover, the second is irrational in its combining a common with a decimal fraction. The three determinations differ in units' place ; hence, we are not sure of units' place. We must accordingly drop the entire decimal part of the average number ; but as the decimal is greater than 0.5, it is customary to change the figure 4 in the average to 5, so that the average is 1685. If the decimal had been less than 5, it would have been dropped, and the average would have remained 1684.

Again, suppose that in three weighings of a dish the following results were obtained : 24.33 *g.*, 24.35 *g.*, and 24.32 *g.*. The sum of these numbers is 73.00, and their average arithmetically may be 24.3333 + or 24.33⅓, but if the above rules be observed, the average must be 24.33. It is to be noted that the sum is given as 73.00 and not as 73. By writing the two ciphers in the decimal we indicate that we know that the tenths and hundredths are zero, while the 73 without the ciphers leaves us in doubt.

Let another illustration emphasize this last point. Suppose the weight of a vessel be found on a balance sensitive to a hundredth of a gram, but that neither the tenths nor the hundredths gram-weights are needed to secure equilibrium. If only the ten- and two-gram weights are on the pan of the balance, its weight is written 12.00 *g.* and not just 12 *g.*. The ciphers indicate the degree of accuracy attained. They mean that the tenths and hundredths were tried in determining the weight, but were not needed. By expressing a weight as 12.00 *g.* you indicate that a balance sensitive to hundredths of grams was used, while 12.0 *g.* would mean that a balance sensitive only to tenths of grams was employed.

In the directions for the quantitative experiments the degree of accuracy is denoted by the number of decimal places kept in specifying a quantity to be taken. Thus, in Experiment 46, exactly 2.00 *g.* are specified, which means that on a balance sensitive to hundredths of grams, two grams, and not more or less by a hundredth of a gram, are to be taken. In Experiment 16 the directions are to take about 5 *g.* of manganese dioxid. This quantity may be weighed roughly, that is, to about a gram, it making no difference if 4 *g.* or 6 *g.* should happen to be taken. If the amount had been written 5.0 *g.*,

it would have been necessary to use a more sensitive balance and weigh to tenths of grams.

Suppose that it were found that 2.68 *g.* of oxygen occupied a volume of 1,871 *c.c.*, *i. e.*, 1.871 *l.* Then the quotient of 2.68 divided by 1.871 gives the weight of one liter. The question arises : How many figures of the quotient are to be retained? It is apparent that if only weighings to hundredths of grams were made, then only hundredths should be kept. Accordingly the quotient is 1.43.

Arithmetical operations on data obtained in quantitative experiments may be much abbreviated, with no loss in accuracy, by dropping after an operation of multiplication or division all except the significant figures in a number.

To illustrate, let us solve the following problem : Find the reduced volume of 283 *c.c.* of a gas measured at 662 *mm.* and 22°.

It is to be noted that no one of the three numbers given has more than three figures; hence, there are only three significant figures. Substituting in the formula (§ 27), we have

$$V = 283 \left(\frac{273}{760} \times \frac{662}{295} \right)$$

Below are given two calculations of the value of V, the one to the right retaining all figures after each multiplication, the one to the left retaining in each product only three (significant) figures.

283	283
273	273
849	849
1981	1981
566	566
77259	77259

$$
\begin{array}{r}
773 \\
662 \\
\hline
1546 \\
4638 \\
4638 \\
\hline
511726
\end{array}
\qquad
\begin{array}{r}
77259 \\
662 \\
\hline
154518 \\
463554 \\
463554 \\
\hline
51145458
\end{array}
$$

$$
\begin{array}{r}
295 \\
760 \\
\hline
17700 \\
2065 \\
\hline
224200
\end{array}
\qquad
\begin{array}{r}
295 \\
760 \\
\hline
17700 \\
2065 \\
\hline
224200
\end{array}
$$

$$
224)\ 512(228.5
$$
$$
\begin{array}{r}
448 \\
\hline
640 \\
448 \\
\hline
1920 \\
1792 \\
\hline
1280
\end{array}
$$

$$
224200)\ 51145458\ (228.1
$$
$$
\begin{array}{r}
4484 \\
\hline
6305 \\
4484 \\
\hline
18214 \\
17936 \\
\hline
2785
\end{array}
$$

As is seen, the reduced volumes differ only in the first decimal place. But as the units are doubtful, the tenths are not significant. As the tenths in 228.5 is 0.5, the number according to custom is increased to 229. It is thus manifest that the abbreviated operations give as good results as the detailed one.

FORMS OF RECORD OF DATA

It always saves time and energy to enter data as soon as obtained in some approved tabular form. Always use a note book, never a scrap of paper. Preserve all the arithmetical work so that, if necessary, it may be checked up with a second determination. Some forms of tabular entries are given at the end of the directions

for the performance of various experiments. A very common operation in quantitative work is the following :

A dish or other vessel is weighed, some substance placed in it, and a second weighing made. The difference in the weights gives the weight of the substance. A good form of record for this operation is this :

```
Wt. of dish, crucible, or test tube + substance ........ = 47.63g.
Wt.    "                                          ........ = 23.42g.
Wt. of substance ..................................... = 24.21g.
```

Suppose a substance is being heated to constant weight in an evaporating dish. A convenient form of record is the following :

```
Wt. of dish + substance after heating for 20 min. ..... = 47.84g.
Wt.   "   +    "        "       "    "  10  "   more = 47.67g.
Wt.   "   +    "        "       "    "  10  "    "  = 47.63g.
Wt.   "   +    "        "       "    "  10  "    "  = 47.63g.
Wt.   "                                          ........ = 23.42g.
Wt. of substance ..................................... = 24.21g.
```

Other similar forms may be readily devised by the student. It is a good plan to decide upon what form of record is to be used before commencing a quantitative experiment. The very preparation of a form often helps wonderfully in keeping track of the steps in an experiment.

LABORATORY EQUIPMENT

The subjoined lists contain the apparatus and the chemicals required for the experiments in this book. Prices and quantities have not been given, but the author will be pleased to give information to teachers using the book as to the quantities of apparatus and chemicals used by his own classes. Prices may be obtained from any of the dealers in chemical supplies.

LIST A

INDIVIDUAL APPARATUS

This list comprises the pieces of apparatus constantly used by a single student, who should be provided with each piece.

6 Test tubes, 4 x ½".	1 Iron tongs.
6 Test tubes, 6 x ¾".	1 Platinum wire.
2 Test tubes, 9 x 1".	1 Blowpipe.
1 Beaker, 100 c. c.	1 Iron forceps.
1 Beaker, 250 c. c.	1 ¹Triangular file, 6".
1 Flask, 100 c. c.	1 ¹Round file, 8".
1 Flask, 250 c. c.	1 Wire gauze or asbestos board.
1 Retort, 250 c. c.	1 ¹Wing-top burner.
3 Glass plates, 4 x 4".	1 Mortar and pestle, 4".
1 Thistle tube.	1 Iron spoon.
1 Funnel, 2½".	1 ²Deflagrating spoon.
1 ¹Porcelain crucible, 1 oz.	1 ²Glass rod, 5".
1 ¹Pipestem triangle.	1 Two-hole rubber stopper to
1 Evaporating dish, 3".	fit large test tubes.
1 ²Test-tube holder.	3 ft. rubber tubing, ³⁄₁₆".
1 ²Test-tube brush.	3 ft. glass tubing, medium wall,
1 Test-tube rack.	to fit rubber stopper.

---

1 These pieces of apparatus may be used by several students in common.
2 These pieces of apparatus may readily be made by the student himself.

LIST B

Table Apparatus

This list includes the apparatus which should be kept at the laboratory desk used by the student or on a side table. It is a part of the equipment to be used by different classes.

1 Retort stand with two rings and a clamp.
6 Wide-mouthed bottles or receivers.
1 Pneumatic trough.
1 Bunsen burner.
3 ft. rubber hose for attaching Bunsen burner.
1"Acid bottles."
1Assorted corks.
1Hofmann screw-cocks.
1Mohr pinch-cocks.
1Iron and copper wire.
1Sand.
1Graduated cylinders, 100 c. c. and 500 c. c.
1Bar magnets.
1Splinters of wood.
1Wax tapers.
1Meter sticks.
1Trip scales and weights.
1Chaslyn balances.

1 It is not feasible to give quantities for these articles; as many as possible should be provided, although it is possible to get along with few.

LIST C

Demonstration Apparatus

This list comprises the apparatus which the teacher should have for demonstrating experiments. It should be of the best quality and not mere makeshift.

1 Eudiometer and trough.
1 Electrolysis of water apparatus.
1 Safety tube.
1 Kipp's gas generator (it is well to have two or three all charged and ready to deliver at any time such gases as hydrogen, carbon dioxid, etc.).
2 U-tubes, 6″ and 8″.
1 Liebig's condenser.
1 Thermometer.
1 Bulb tube.
1 Induction coil.
1 Battery to run coil.
1 Large lamp chimney.
1Rubber stoppers of various sizes.
1Ignition tubes.
1Supply of glass tubing of various sizes.
1Supply of rubber tubing of various sizes.

1 Refer to note in List B.

LIST D

CHEMICALS

The chemicals should as far as possible be of "c. p." grade.

Acid, acetic.
citric.
hydrochloric.
nitric.
oxalic.
pyrogallic.
sulfuric.
tartaric.
Alcohol, ethyl.
methyl.
Alum, chrome.
potash.
Aluminum, metal.
sulfate.
Ammonium, chlorid.
hydroxid.
nitrate.
oxalate.
sulfid.
Antimony, metal.
Arsenic, metal.
Arsenious oxid.
Asbestos.
Barium, chlorid.
nitrate.
Bismuth, metal.
nitrate.
Bleaching powder.
Borax.
Cadmium chlorid.
Calcium, carbid.
carbonate (marble).
chlorid.
fluorid.
oxid (lime).
sulfate (gypsum).

Carbon bisulfid.
Charcoal, animal.
wood.
Coal, hard.
soft.
Cobalt, chlorid.
nitrate.
Cochineal.
Copper, metal.
nitrate.
sulfate.
Ether.
Glycerin.
Indigo.
Iodin.
Iron, metal (filings and wire).
chlorid.
sulfate.
sulfid.
Lead, metal.
nitrate.
monoxid (litharge).
red.
Litmus,
paper.
Magnesium, metal (powdered and ribbon).
sulfate.
Manganese, dioxid.
sulfate.
Mercury.
Mercuric chlorid.
nitrate.
oxid.
Mercurous nitrate.
Nickel chlorid.

Phenolphthalein.
Picture cord (iron).
Potassium, metal.
    bromid.
    carbonate.
    chlorate.
    chromate.
    dichromate.
    ferricyanid.
    ferrocyanid.
    hydroxid.
    iodid.
    permanganate.
    sulfate.
    sulfocyanid.
Rosin.
Silver nitrate.
Soda-lime.

Sodium, metal.
    bicarbonate.
    carbonate.
    chlorid.
    hydroxid.
    nitrate.
    phosphate.
    silicate.
    sulfate.
    sulfite.
Stannous chlorid.
Starch.
Strontium nitrate.
Sulfur, flowers and roll.
Tin, granulated.
Vaseline.
Zinc, granulated and sheet.
    sulfate.

APPENDIX G

REFERENCE BOOKS

DICTIONARIES

COMEY, Arthur Messinger. Dictionary of Chemical Solubilities. *New York: The Macmillan Co. $5.00.*

HOPKINS, Albert A. Scientific American Cyclopedia of Receipts. *New York: Munn & Co. $5.00.*

WATTS, Henry. Dictionary of Chemistry. Revised by Morley and Muir. *New York: Longmans, Green & Co. 4 vols. $65.00.*

DESCRIPTIVE CHEMISTRY

HOLLEMAN. Inorganic Chemistry. Trans. by Cooper. *New York: John Wiley & Sons. $2.50.*

JONES, Harry C. Principles of Inorganic Chemistry. *New York: The Macmillan Co. $4.00.*

MENDELEEFF, Dimitry Ivanovitch. Principles of Chemistry. *New York: Longmans, Green & Co. 2 vols. $10.00.*

NEWTH, G. S. Text-book of Inorganic Chemistry. *New York: Longmans, Green & Co. $1.75.*

OSTWALD, Wilhelm. The Principles of Inorganic Chemistry. *New York: The Macmillan Co. $6.00.*

REMSEN, Ira. Chemistry. (Advanced Course.) *New York: Henry Holt & Co. $2.80.*

ROSCOE, Sir Henry Enfield & Schorlemmer, C. Treatise on Chemistry. (First two Volumes.) *New York: D. Appleton & Co. $15.00.*

THEORETICAL AND PHYSICAL CHEMISTRY

DOBBIN, L. & Walker, J. Chemical Theory for Beginners. *New York: The Macmillan Co. 70 cents.*

JONES, Harry C. Elements of Physical Chemistry. *New York: The Macmillan Co. $4.00.*

VAN DEVENTER, Charles. Physical Chemistry for Beginners. Trans. by Boltwood. *New York: John Wiley & Sons. $1.50.*

WALKER, James. Introduction to Physical Chemistry. *New York: The Macmillan Co. $3.00.*

HISTORICAL CHEMISTRY

LADENBURG, Dr. A. Lectures of the History of the Development of Chemistry Since the Time of Lavoisier. Trans. by Dobbin. *Chicago: The University of Chicago Press. $1.75.*

MEYER, Ernest von. History of Chemistry. Trans. by G. McGowan. *New York: The Macmillan Co. $4.50.*

MUIR, Matthew Moncrieff Pattison. Heroes of Science, Chemists. *New York: Thomas Nelson & Sons. $1.50.*

RAMSAY, W. Gases of the Atmosphere. *New York: The Macmillan Co. $2.00.*

THORPE, Thomas Edward. Essays in Historical Chemistry. *New York: The Macmillan Co. $2.25.*

VENABLE, Frank Preston. Short History of Chemistry. *Boston: D. C. Heath & Co. $1.00.*

VENABLE, Frank Preston. Development of the Periodic Law. *Easton, Pa.: Chemical Publishing Co. $2.50.*

ALEMBIC Club Reprints. *Chicago: The University of Chicago Press. 40 cents each.*

REPRINTS of Science Classics. *Chicago: The School Science Press. 5 and 10 cents each.*

ORGANIC CHEMISTRY

BERNTHSEN, A. Text-book of Organic Chemistry. Trans. by McGowan. *New York: D. Van Nostrand Co. $2.50.*

GATTERMANN, Ludwig. Practical Methods of Organic Chemistry. Trans. by Shober. *New York: The Macmillan Co. $1.60.*

LASSAR-COHN. Laboratory Manual of Organic Chemistry. Trans. by Smith. *New York: The Macmillan Co. $2.25.*

ORNDORFF, W. R. Laboratory Manual in Organic Chemistry. *Boston: D. C. Heath & Co. 35 cents.*

REMSEN, Ira. Organic Chemistry. *Boston: D. C. Heath & Co. $1.20.*

RICHTER, Victor von. Organic Chemistry. Trans. by Smith. *Philadelphia: P. Blakiston Son & Co. 2 vols. $6.00.*

INDUSTRIAL AND ANALYTICAL CHEMISTRY

JULIAN, Frank. Quantitative Chemical Analysis. *St. Paul: The Ramsey Publishing Co. $6.00.*

THORP, Frank Hall. Outlines of Industrial Chemistry. *New York: The Macmillan Co. $3.50.*

WAGNER, Rudolph Johannes. Manual of Chemical Technology. *New York: D. Appleton & Co. $1.50.*

ALUMINUM and Aluminum Alloys. *Pittsburg, Pa.: The Pittsburg Reducing Co. $1.50.*

MISCELLANEOUS

DANA, Edward Salisbury. Minerals and How to Study Them. *New York: John Wiley & Sons. $1.50.*

GREENE, H. Coal and Coal Mines. *Boston: Houghton, Mifflin & Co. 75 cents.*

HARDIN, Willett L. Rise and Development of Liquefaction of Gases. *New York: The Macmillan Co. $1.50.*

HOPPING. The Practical Study of Common Minerals. *Chicago: The School Science Press. 60 cents.*

JOHNSTON, James Finlay Weir. Chemistry of Common Life. *New York: D. Appleton & Co. $2.00.*

KIMBALL, Arthur L. Physical Properties of Gases. *Boston: Houghton, Mifflin & Co. $1.25.*

LASSAR-COHN. Chemistry in Daily Life. Trans. by Muir. *Philadelphia: J. B. Lippincott & Co. $1.50.*

SHENSTONE, William Ashwell. Methods of Glass-Blowing. *New York: Longmans, Green & Co. 50 cents.*

THORP, Frank Hall. Inorganic Chemical Preparations. *Boston: Ginn & Co. $1.50.*

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